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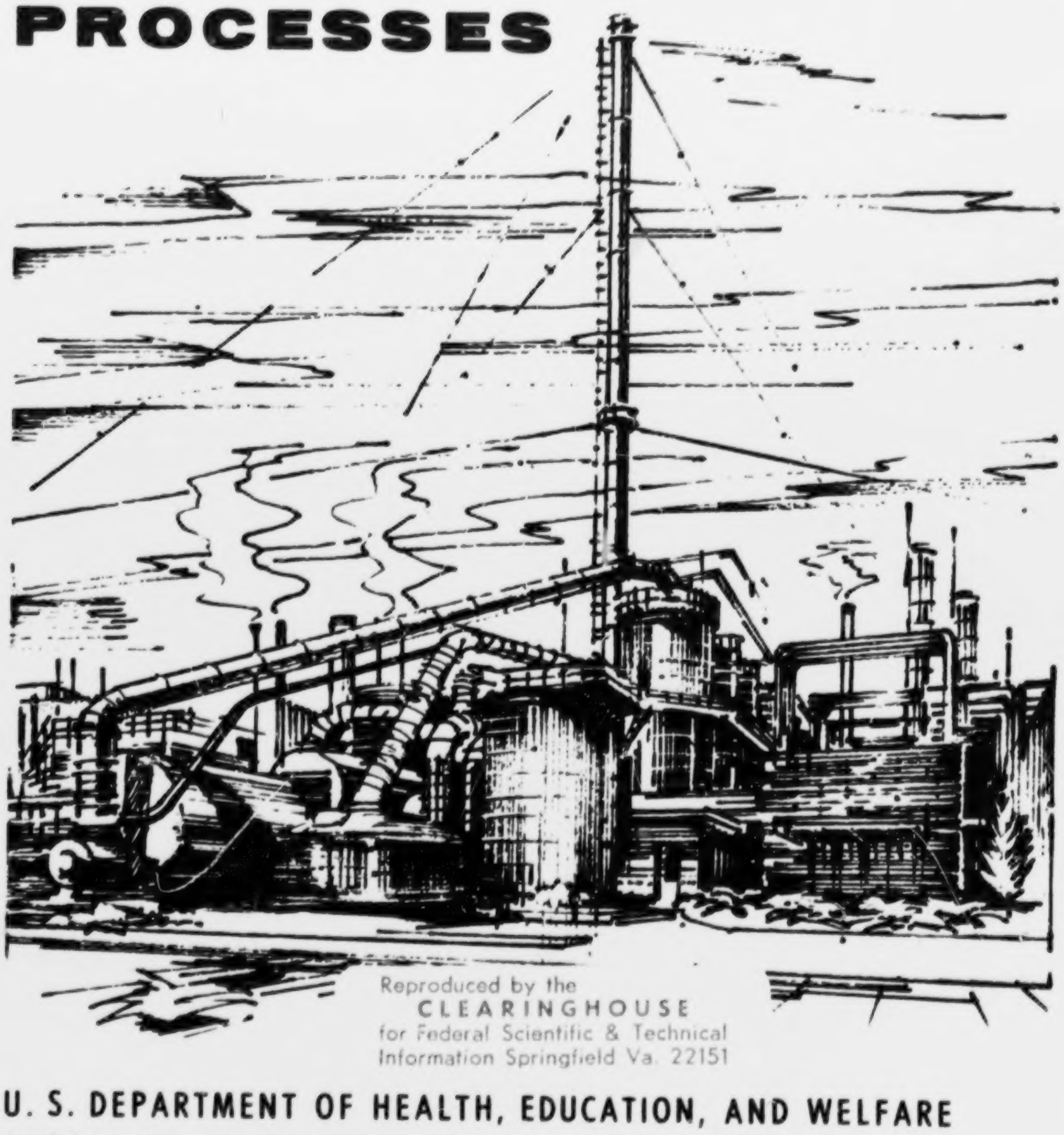
# ATMOSPHERIC EMISSIONS FROM SULFURIC ACID MANUFACTURING PROCESSES



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U. S. DEPARTMENT OF HEALTH, EDUCATION, AND WELFARE
Public Health Service

136

# ATMOSPHERIC EMISSIONS FROM SULFURIC ACID MANUFACTURING PROCESSES

**Cooperative Study Project**
**Manufacturing Chemists' Association, Inc.**
**and**
**Public Health Service**

**U. S. DEPARTMENT OF HEALTH, EDUCATION, AND WELFARE**
**Public Health Service**
**Division of Air Pollution**
**Cincinnati, Ohio**
**1965**

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# PREFACE

To provide reliable information on the nature and quantity of emissions to the atmosphere from chemical manufacturing, the Manufacturing Chemists' Association, Inc. and the Division of Air Pollution, Public Health Service, United States Department of Health, Education, and Welfare, entered into an agreement on October 29, 1962. A cooperative program was established to study emissions from selected chemical manufacturing processes and publish information about them in a form helpful to air pollution control and planning agencies and to chemical industry management. Direction of these studies is vested in an MCA-USPHS Steering Committee, presently composed as follows:

| *Representing USPHS:* | *Representing MCA:* |
|---|---|
| John H. Ludwig* | Willard F. Bixby* |
| Austin N. Heller | Louis W. Roznoy |
| Robert Porter | Clifton R. Walbridge |
| Andrew H. Rose, Jr. | Elmer P. Wheeler |

Information to be published will describe the range of emissions during normal operating conditions and the performance of established methods and devices employed to limit and control these emissions. Interpretation of emission values in terms of ground-level concentrations and assessment of potential effects produced by the emissions are both outside the scope of this program.

This report deals with emissions from sulfuric acid manufacture, the first study to be made under the joint program. Sulfuric acid manufacture was chosen because it represents an important segment of the chemical manufacturing industry in the United States, involves plants in many parts of the country, and has well-recognized air pollution potential(*1*).

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*Principal representatives .

## ACKNOWLEDGMENTS

Many companies and individuals in the sulfuric acid industry have been helpful in carrying forward this study, and for their contributions the project sponsors extend sincere gratitude.

Special thanks are due the following organizations for their participation in a program of stack sampling and analysis specifically for this study:

The American Agricultural Chemical Company
American Cyanamid Company
Chemical Construction Corporation
E. I. du Pont de Nemours & Co.
V-C Chemical Company — Division of Socony Mobil Oil Company

Several companies also provided from their records, either directly or through the air pollution control districts of Los Angeles County and the San Francisco Bay Area, additional stack sampling and analytical data, which have been incorporated into the report. Other companies contributed valuable assistance to the project. Among those are:

Allied Chemical Corporation
The American Agricultural Chemical Company
Collier Carbon and Chemical Corporation
Monsanto Company
Stauffer Chemical Company
U. S. Phosphoric Products Division, Tennessee Corporation

Stanley T. Cuffe of the Public Health Service and Carlton M. Dean of Monsanto Company were the investigators in the study and are the principal authors of this report. The sponsors acknowledge the contribution of Monsanto Company in providing the services of Mr. Dean, who assembled much of the technical information.

# USE AND LIMITATION OF THE REPORT

This report has been prepared to provide reliable information on atmospheric emissions from sulfuric acid manufacturing plants and on methods and equipment normally employed to limit these emissions to satisfactory levels.

Background information is included to define the importance of the sulfuric acid industry in the United States. Basic characteristics of the industry are discussed, including growth rate in recent years, types of raw materials used, end uses for the product, and the number of producing establishments, i.e. manufacturing sites, in existence during the past and at the present time.

Process descriptions are given for the two processes in commercial use: the contact process and the chamber process. Process information includes discussions of the normal process variables that affect the types and quantities of emissions, the normal range of emissions, startup and shutdown losses, and methods of emission control and recovery. Supplemental material provides detailed descriptions of sampling and analytical methods.

The emission data represent results from approximately 12 percent of the present number of establishments.* Most of these data have been gathered from production records of sulfuric acid producers. The data also include results from several stack-sampling programs conducted jointly during 1963 by the Manufacturing Chemists' Association and the United States Public Health Service. One contact plant and two chamber plants were included in this sampling program. Results obtained from these tests are consistent with the values of the emissions reported from other sources.

The manufacture of sulfuric acid has been a basic industry in the United States for many years, and the manufacturing procedures have become well-established. Based on this fact and the indication that the industry growth in recent years closely parallels the growth curve of the general economy, it is likely that the information provided in this report will be characteristic of the industry for at least 5 years and possibly for 10 years.

Over a long period of years, the number of contact plants has increased while the number of chamber plants has decreased. During the mid-1940's, the number of establishments producing sulfuric acid by the chamber process was approximately equal to the number producing acid by the contact process. Today more than twice as many establishments use the contact process. This trend indicates that the contact process will continue to gain in importance on a nationwide basis.

Emissions to the atmosphere from a sulfuric acid plant depend upon a number of factors, such as design of the plant, skill of operation, efficiency of the catalyst, completeness of recovery operations, and the use of special devices to reduce emissions. As our technology progresses, we can logically expect that improvements will make it feasible to reduce emissions from sulfuric acid plants. A review of the industry in 5 to 10 years should indicate whether the data presented in this report are still representative or should be updated to reflect the then-prevailing conditions.

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*Establishment: a works in which there may be one or more sulfuric acid plants or units, each being a complete production entity.

Although this report has been prepared as an industry review primarily for public officials concerned with the control of air pollution, we expect that the information will also be helpful to chemical plant management and technical staffs. It may aso be helpful to engineering students, medical personnel, and other professional people interested in emissions from sulfuric acid manufacturing plants.

# SUMMARY

## SULFURIC ACID PRODUCTION

In 1963 production of sulfuric acid in the United States was approximately 20,500,000 tons(2). Based on the 24.4 percent increase in production from 1956 to 1963, the expected average growth for the next 5 years should be 3 to 4 percent per year.

All sulfuric acid is made by either the chamber or the contact process. The 163 contact establishments account for about 90 percent of the U. S. production. The 60 chamber establishments account for the balance of U. S. production. Products include 50° to 66° Bé (62 to 93 percent acid), 98 to 99 percent acid and up to 100 percent oleum, i.e. 100 percent sulfur trioxode(2).

Elemental sulfur, or any sulfur-bearing material, is a potential raw material for both chamber and contact processes. Elemental sulfur accounts for about 75 percent of all raw materials used in sulfuric acid production. Most of the remaining new acid comes from pyrites or other iron sulfides; zinc, copper and lead ores; smelter gas; hydrogen sulfide; and crude sulfur. Substantial quantities of "fresh clean acid" are made by regeneration or decomposition of spent acid from petroleum refineries or other chemical processes.

## EMISSIONS FROM SULFURIC ACID MANUFACTURE

### Chamber Plants

The primary source of emissions in the chamber process is the final Gay Lussac tower. Emissions include nitrogen oxides, sulfur dioxide, and sulfuric acid mist and spray.

Concentrations of total nitrogen oxides in these exit gases range from about 0.1 to 0.2 volume percent. Sulfur dioxide concentrations occur in the same range. About 50 to 60 percent of the total nitrogen oxides is nitrogen dioxide, which characterizes the exit gas by a reddish-brown color.

Combined sulfuric acid mist and spray in the exit gas varies from 5 to 30 milligrams per cubic foot. The sulfuric acid mist contains about 10 percent dissolved nitrogen oxides. Over 90 percent of the acid mist particles are larger than 3 microns diameter.

### Contact Plants

The major source of emissions from contact sulfuric acid plants is the exit gas from the absorber. This gas contains unreacted sulfur dioxide, sulfuric acid spray and mist, and unabsorbed sulfur trioxide. Trace amounts of nitrogen oxides may also be present under some conditions, e.g. use of a raw material feed containing nitrogen compounds.

Unconverted sulfur dioxide gas, which is colorless, passes through the absorption system and is discharged to the atmosphere. The quantity of this gas emitted is a direct function of the degree of conversion of sulfur dioxide to sulfur trioxide and may vary from 0.1 to 0.5 percent by volume of the stack gases. During startup or during some emergency shutdowns, higher concentrations will occur.

Emissions of sulfuric acid mist and spray usually vary from 3 to 15 milligrams per standard cubic foot of gas; values ranging from as low as 1 to as high as 50 milligrams per standard cubic foot have been observed. The appearance of a dense white plume at the absorber exit stack indicates the presence of a substantial number of small particles (i.e. less than 3 microns in diameter) and does not necessarily reflect the concentration of sulfuric acid mist present.

Unabsorbed sulfur trioxide usually constitutes a small part of the absorber exit gas. When discharged to the atmosphere it is hydrated and forms a visible white plume of acid mist. Although the concentration of unabsorbed sulfur trioxide can vary appreciably, from 0.5 to 48 milligrams per standard cubic foot of gas, it is usually closer to the lower figure and is a small part of the total acid mist emission.

### Acid Concentrators

Emissions of sulfuric acid mist may originate from the operation of either vacuum-type or drum-type concentrators of dilute acid. Significant emissions are unlikely with the vacuum type, however.

### Minor Losses

Minor amounts of sulfur oxides may be emitted to the atmosphere from tank car and drum-loading operations, and from storage tank vents. Oxides of nitrogen may be emitted from process acid tanks in the chamber process. Wind may cause losses of solid sulfur or sulfide ores from storage piles.

## CONTROL OF EMISSIONS

### Chamber Plants

The most important factors in minimizing emissions to the atmosphere in chamber plants are selection of raw materials, skill of operation, and preventive maintenance. Recovery equipment following the final Gay Lussac tower is rarely employed. In one known instance, however, water-scrubbing the exit gases reduced the sulfur dioxide by 40 percent and the oxides of nitrogen by 25 percent.

### Contact Plants

As with chamber plants, selection of raw materials, quality of plant design, skill of operation, and preventive maintenance are the principal factors in the control of emissions from contact plants. When contact plants operate at excessively high throughput rates, a substantial increase in emissions may be expected.

Although processes are available for recovering 70 to 90 percent or more of the unconverted sulfur dioxide in the stack gases, these are generally uneconomical. Plants have used the "Cominco"® ammonia scrubbing process for reducing the concentration of sulfur dioxide to about 0.08 percent in a single stage and to 0.03 percent in two stages. This process removes little or no acid mist. Economical disposal of byproduct ammonium sulfate may be a problem.

Control devices currently used for minimizing emissions of acid mist and spray are electrostatic precipitators and glass-fiber and wire-mesh eliminators. Electrostatic devices are highly efficient regardless of acid-mist particle size and are capable of reducing mist emissions by 92 to 99.9 percent.

The collection efficiencies for glass-fiber acid-mist eliminators range from 94 to 99.99 percent. These high efficiencies can be maintained at variable tail-gas flow rates in collection of acid-mist particles smaller than 3 microns in diameter.

Stainless steel wire-mesh eliminators for acid mist and spray provide low first cost but are susceptible to corrosion by concentrated sulfuric acid. A typical installation may show 93 percent collection efficiency for acid mist during the production of 98 percent acid. When oleum is produced, the proportion of acid-mist particles smaller than 3 microns in diameter is higher; collection efficiency decreases sharply and may be less than 40 percent.

In some cases tall stacks, 150 feet or higher, are used to disperse exit gases from the absorber into the atmosphere. In addition, there is some evidence that the walls of the stacks collect large acid particles and thus reduce the acid-spray emissions to atmosphere.

## EMISSION GUIDELINES

### Contact Plants

The tabulations of emission and operating data in Tables A2 and A3 show that many contact sulfuric acid plants operate at between 97 and 98 percent efficiency for conversion of sulfur dioxide. It is practical, therefore, to design and operate new contact plants for such efficiencies. Note, however, that the concentration of sulfur dioxide in the tail gas from one plant having a conversion efficiency of 97 percent can be higher or lower than that from a second plant also having a 97 percent conversion efficiency. This variation in the concentration of sulfur dioxide in tail gases is dependent upon the concentration of sulfur dioxide in the feed gas to the converter.

The data in Table A3 show that it is possible to recover 99 percent of all of the emissions of acid spray and mist by adding commercially available mist eliminators. No appreciable difference in ranges of acid-mist concentrations is apparent for different types of contact sulfuric acid plants. Whether a plant is a sulfur-burning type, with or without air dilution, or is a metallurgical or spent-acid type does not appear to affect significantly the concentrations of acid mist in the stack gas from an absorber.

Excessive sulfur dioxide emissions during cold startups of contact units can be reduced appreciably by bringing the plant and catalyst to conversion temperatures before admitting sulfur dioxide gas to the converter and by increasing feed rate gradually.

### Chamber Plants

The tabulations for two sulfur-burning plants in Table A1 indicate much lower concentrations of sulfur dioxide in the stack gases than in most contact plants. Conversion efficiencies appear to be higher than 98 percent; however, when raw materials other than sulfur are used, conversions are lower.

Losses of acid mist and spray were as high as 33 milligrams per standard cubic foot of stack gas. More than 90 percent of the particles were larger than 3 microns.

While sulfur dioxide losses from chamber plants are lower than for contact plants, the stack gases contain substantial amounts of nitrogen oxides, a condition that does not exist in contact plants. Total nitrogen oxide emissions from the two sulfur-burning plants tested averaged 0.14 percent, expressed as nitrogen dioxide ($NO_2$), of which half to two-thirds was in the form of $NO_2$ and the balance was nitric oxide (NO).

Auxiliary equipment is rarely installed for elimination of the sulfur dioxide and the nitrogen oxide components.

## GROWTH OF SULFURIC ACID INDUSTRY

Over a long period of years, sulfuric acid production has grown at essentially the same rate as the general economy. While some uses of the product have declined, compensating new uses have been introduced. The over-all average growth rate has been 3½ to 4 percent per year since 1950. Table 1 shows growth in acid production and in number of producing establishments for certain years since 1939.

TABLE 1. GROWTH OF SULFURIC ACID INDUSTRY IN THE UNITED STATES(*2*)

| | Production thousands of short tons (Basis: 100% $H_2SO_4$) | | Number of producing establishments | | | |
|---|---|---|---|---|---|---|
| Year | New acid | Total acid[a] | Contact only | Chamber only | Both | Total |
| 1939 | 4,795 | 4,795 | 58 | 83 | 12 | 153 |
| 1945 | 8,687 | 9,522 | | | | |
| 1949 | 10,727 | 11,432 | 94 | 83 | 10 | 187 |
| 1951 | 12,389 | 13,372 | | | | |
| 1956 | 15,737 | 16,494 | 131 | 74 | 6 | 211 |
| 1960 | 17,085 | 17,883 | | | | |
| 1961 | 17,058 | 17,848 | 144 | 65 | 5 | 214 |
| 1962 | 18,433 | 19,351 | | | | |
| 1963[b] | 19,614 | 20,513 | 155 | 58 | 2 | 215 |

[a] Including fortified spent acid.
[b] Preliminary data.

Of interest is the 330 percent increase in acid production since 1939, with only a 40 percent increase in the total number of establishments. Average production has increased from 31,400 tons in 1939 to 95,000 tons in 1963. Furthermore, almost all of the new plants built use the contact process.

Another significant change is the reduction in the ratio of production for merchant sales to production for captive use. In 1939 this ratio stood at 2:1 (merchant sales: captive), whereas it is now closer to 1:1.

In recent years, 6 to 7 percent of the total production of new sulfuric acid has been derived from copper, lead, and zinc smelter gases. This production is summarized in Table 2.

Although figures are not available, probably larger amounts of acid than heretofore are presently derived from recovered hydrogen sulfide formerly flared in refinery stacks.

Another source of acid production is domestic and imported pyrites, which are estimated to have accounted for some 1,600,000 short tons of acid in 1962.

The importance of various regions of the country as acid-producing areas is also changing. Table 3 illustrates this change for the period 1956 to 1963, and compares current capacity with production.

TABLE 2. PRODUCTION OF BYPRODUCT SULFURIC ACID FROM COPPER, ZINC, AND LEAD PLANTS IN THE UNITED STATES(3)

| Years | Production, thousands of short tons[a] (Basis: 100% $H_2SO_4$) | | |
|---|---|---|---|
| | Copper plants[b] | Zinc plants[c] | Total |
| 1954-1958 (Avg) | 393 | 759 | 1,152 |
| 1959 | 282 | 804 | 1,086 |
| 1960 | 413 | 771 | 1,184 |
| 1961 | 363 | 776 | 1,139 |
| 1962 | 404 | 815 | 1,219 |
| 1963 | 359 | 862 | 1,220 |

[a] Includes acid from foreign material.

[b] Includes acid produced at a lead smelter.
Excludes acid made from pyrites concentrates in Arizona, Montana, Tennessee, and Utah.

[c] Excludes acid made from native sulfur.

TABLE 3. CAPACITY AND PRODUCTION OF SULFURIC ACID IN THE UNITED STATES BY REGIONS(2)

| Region | Capacity[a] (Jan. 1963), thousands of short tons | Production of new acid, thousands of short tons (Basis: 100% $H_2SO_4$) | | | Indicated operation 1962, % |
|---|---|---|---|---|---|
| | | 1956 | 1962 | % Change | |
| New England | 279 | 201.8 | 184.1 | — 8.8 | 66.0 |
| Middle Atlantic | 3.546 | 2,392.5 | 2,481.8 | + 3.7 | 70.0 |
| South | 12,788 | 7,996.0 | 9,625.8 | +20.4 | 75.3 |
| North Central | 5,559 | 3,516.7 | 3,818.6 | + 8.6 | 68.7 |
| Mountain, Pacific and Hawaii | 3,567 | 1,630.3 | 2,322.5 | +42.4 | 65.1 |
| | 25,739 | 15,737.3 | 18,432.3 | +17.1 | 71.6 |

[a] Based on industry estimate.

On the basis of tonnage produced, the largest increase has occurred in the South. Most of this increase has been in Florida for production of phosphate fertilizer. On a percentage basis, the Western area has shown the greatest growth. Probably half of its growth has been for metallurgical operations, including uranium concentration in the Rocky Mountain area. Use of acid for uranium recovery has been reduced recently because of the cutback in government procurement. The balance of the growth in the Western area reflects increased use by the oil industry for akylation in California and Washington and increased phosphate fertilizer production.

Estimated distribution of sulfuric acid use by industry is approximately as follows:

| | |
|---|---|
| Fertilizer | 40% |
| Chemicals | 25 |
| Oil refining | 14 |
| Pigments | 6 |
| Iron and steel | 5 |
| Miscellaneous, including rayon and film, metallurgical, and other than iron and steel, etc. | 10 |
| Total | 100% |

Table 3 also compares estimated capacity by region as of January 1, 1963, with 1962 production. Regionally, production varied from a low of about 65 percent of capacity in the Mountain and Pacific states to a high of about 75 percent of capacity in the South.

From the standpoint of air pollution control, the number of companies operating acid plants may be of interest. In 1961:

| | |
|---|---|
| 23 companies operated | 163 establishments |
| 51 companies operated | 51 establishments |
| 74 companies operated a total of | 214 establishments |

Trends of increasing production displayed in the past may be expected to continue. Again, changes in industrial usage may change the area production pattern. Hydrochloric acid could displace sufuric acid in new plants for iron and steel pickling or for phosphate rock digestion, but no large growth in these areas is expected in the immediate future.

# SULFURIC ACID MANUFACTURE

## RAW MATERIALS

Elemental sulfur, or any sulfur-bearing material, is a potential raw material for both chamber and contact processes. Because elemental sulfur of high purity (99.5 percent or more) is plentiful in the U.S. at a reasonable price, it accounts for more than 70 percent of all acid production. Most of the remaining production of new acid comes from pyrites or other iron sulfides: zinc, copper and lead ores; smelter gas; hydrogen sulfide; and crude sulfur ores. Substantial quantities of "fresh clean acid" are also made by regeneration or decomposition of spent acid from petroleum refineries or other chemical processes.

Elemental sulfur of extremely high purity, the predominant raw material, is obtained from two main sources. Most of it is mined by the Frasch process on the Gulf Coasts of Louisiana, Texas, and Mexico. As mined, it contains not more than 0.01 percent ash and 0.05 percent or less to 1.0 percent hydrocarbons, with no free water or acid. If low in organic matter, it is called "bright" sulfur; if high, "dark" sulfur. There is no definite dividing line between "bright" and "dark" sulfur.

Sulfur is delivered to the customer in either molten or solid condition. If molten, the sulfur may be as pure when delivered as when it was mined except for possible traces of hydrogen sulfide. If solid, the sulfur will contain more ash, water, and acid, the amount depending on the degree of exposure en route. If the customer's storage pile is located outdoors, these impurities will increase and may reach 0.02 percent ash and 0.003 percent acid, or more. Nevertheless, when the sulfur is used, it usually contains at least 99.5 percent sulfur, dry basis. Except during a rain, moisture is about 0.1 percent.

While small by comparison with Frasch-process sulfur, substantial amounts of elemental sulfur are recovered from sour natural and refinery gas. Whether it is delivered in molten or solid form, this sulfur is always of higher quality than the Frasch-process sulfur before shipment because it usually contains less than 0.05 percent hydrocarbons, no acid or moisture, and only 0.001 to 0.003 percent ash. As with the Frasch process, if this sulfur is delivered molten it may contain traces of hydrogen sulfide.

Use of elemental sulfur in molten form is rapidly increasing because of its higher purity and possible lower transportation and handling costs. Many plants purchase dark sulfur rather than bright, in spite of its higher hydrocarbon content, because it costs less.

## CHAMBER PROCESS *(4, 5, 6)*

### Introduction

The chamber process now produces approximately 10 percent of sulfuric acid in the United States and is expected to account for less in the future. This process yields relatively weak 60° Bé (77.7 percent) acid. Because this acid is more dilute than acid from the contact process, transportation costs per unit of $H_2SO_4$ are higher. Chamber plants in general are captive and of low capacity. Construction and operating costs are usually higher than for contact plants. For these reasons, the chamber process is tending to become a very small factor in sulfuric acid production.

### Production of Sulfur Dioxide ($SO_2$) for the Process

When elemental sulfur is the raw material, it is introduced directly into a sulfur burner, either in solid or molten form. Air from the atmosphere is supplied to the burner, usually under suction, to produce a gas containing 8 to 12 percent sulfur dioxide at a temperature of 1400 to 1800°F.

If sulfide ores are the raw material, they are roasted, i.e., burned, in special proprietary equipment to produce sulfur dioxide gas at an elevated temperature. The gas often contains less sulfur dioxide than when sulfur is used, and more dust and other impurities. Also, the gas usually varies more in composition. Use of byproduct sulfur dioxide gas presents the same difficulties.

Hydrogen sulfide or spent acid may be burned or decomposed to provide sulfur dioxide gas. Such gas is relatively clean, but care must be taken that all organic impurities are wholly burned to avoid excessive consumption of the gaseous catalyst (nitrogen oxides).

### Description of the Chamber Process

In a typical lead chamber plant, as shown in Figure 1, the hot sulfur dioxide gas from the sulfur burner, ore roaster, or other sulfur dioxide producing equipment flows through a Glover tower, then through several chambers in series, and finally through one or more Gay Lussac towers, from which the waste gas passes through a stack to the atmosphere. If the sulfur dioxide gases are dirty, an electrostatic dust precipitator or cyclone dust collector precedes the Glover tower.

In the Glover tower and ensuing chambers the sulfur dioxide is oxidized in the presence of oxides of nitrogen to sulfur trioxide, which combines with water vapor to form sulfuric acid. The chemical reactions are complex and not yet fully understood. It is known that intermediate compounds are formed that finally decompose to yield sulfuric acid and nitrogen oxides for reuse.

The function of the Gay Lussac towers is to recover the released nitrogen oxides. The final tower is fed with 60° Bé acid from the Glover tower, preferably at no more than 100°F, and the oxides are absorbed to form nitrosylsulfuric acid ($SO_5NH$). Maximum catalyst recovery is achieved if the nitrogen oxides entering the tower are maintained in equimolar proportions of nitric oxide (NO) and nitrogen dioxide ($NO_2$). Because the nitrogen oxides are an important cost item, great stress is laid on maximum recovery. The nitrosulfuric acid is recycled to the Glover tower.

The acid made in the chambers averages 50° to 54° Bé (62.18 to 68.26 percent $H_2SO_4$). It is pumped to the top of the Glover tower, flows through it countercurrently to the hot sulfur dioxide gas, and is thus concentrated to 60° (77.67 percent). The Glover tower decomposes the nitrosylsulfuric acid from the Gay Lussac towers and thus releases the nitrogen oxides for reuse. In addition, the Glover tower cools the hot sulfur dioxide gas. Up to 50 percent of all of the acid produced in the plant is formed in the Glover tower.

The hot 60° Bé acid from the Glover tower is cooled, part is recycled to the Gay Lussac towers, and the rest flows to the storage as the final product.

### Yields and Losses

Sulfur — In a well-operated plant using elemental sulfur as a raw

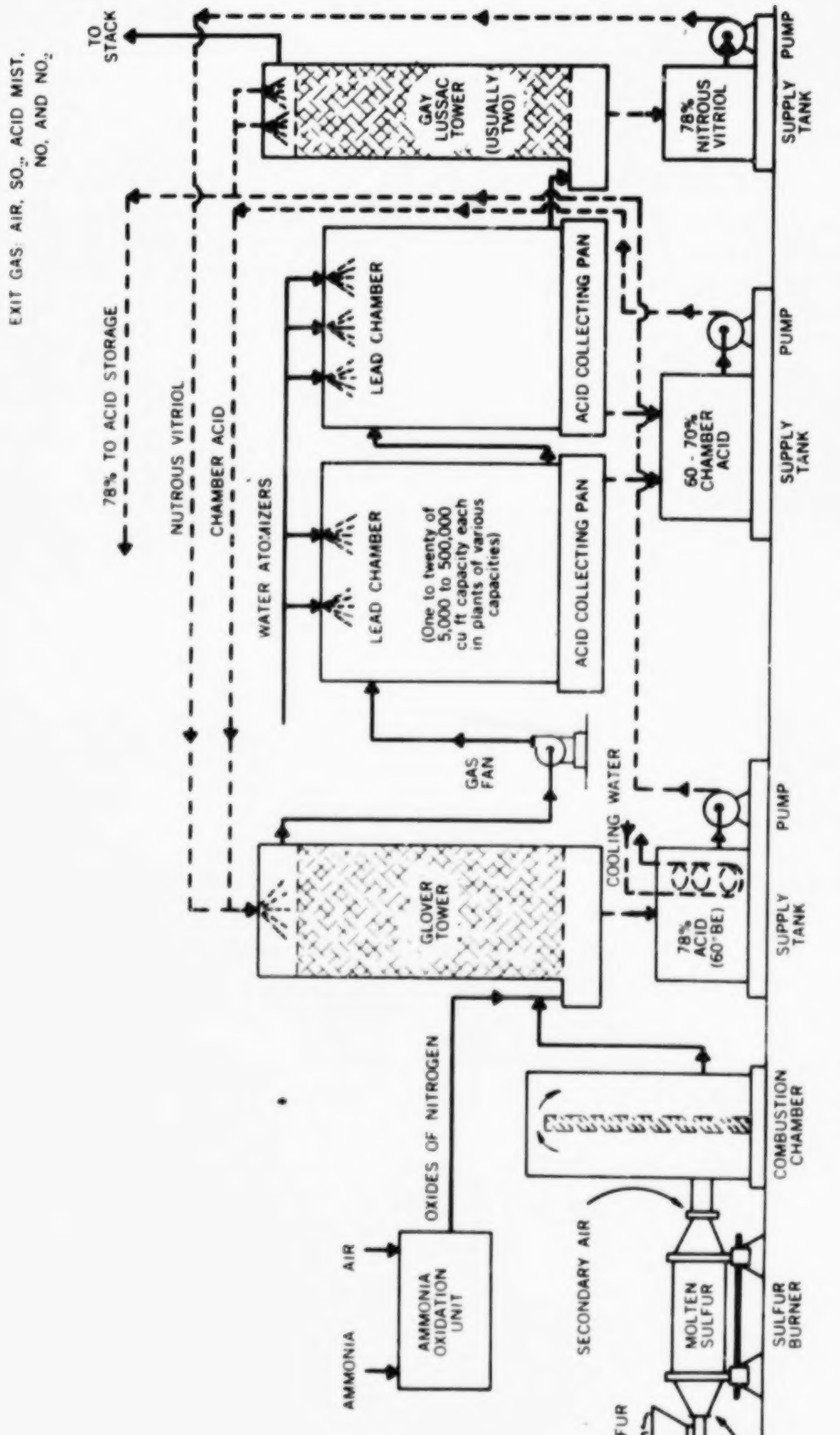

EXIT GAS: AIR, $SO_2$, ACID MIST, NO, AND $NO_2$
TO STACK
78% TO ACID STORAGE
NUTROUS VITRIOL
CHAMBER ACID
WATER ATOMIZERS
GAY LUSSAC TOWER
(USUALLY TWO)
78% NITROUS VITRIOL
SUPPLY TANK
PUMP
LEAD CHAMBER
ACID COLLECTING PAN
60 - 70% CHAMBER ACID
SUPPLY TANK
PUMP
LEAD CHAMBER
(One to twenty of 5,000 to 500,000 cu ft capacity each in plants of various capacities)
ACID COLLECTING PAN
GAS FAN
COOLING WATER
GLOVER TOWER
78% ACID (60°BE)
SUPPLY TANK
PUMP
OXIDES OF NITROGEN
COMBUSTION CHAMBER
AMMONIA
AIR
AMMONIA OXIDATION UNIT
SECONDARY AIR
MOLTEN SULFUR
SULFUR BURNER
SULFUR
PRIMARY AIR

Figure 1 — Simplified flow diagram of typical lead-chamber process for sulfuric acid manufacture (based on use of elemental sulfur as the raw material).

material, yield is usually at least 98 percent. In plants using other raw materials, a yield of 96 percent is considered satisfactory. A yield of 100 percent is practically impossible because of such factors as chemical equilibria, absorption efficiency, and purity of raw materials.

Niter (Nitrogen Oxides) — Loss of niter, i.e., nitrogen oxides, is often expressed in pounds of 96-percent-pure nitrate of soda used per 100 pounds of sulfur burned. Nitrate of soda is rarely used today as a source of the nitrogen oxides; nitric acid or ammonia, usually the latter, has taken its place. When sulfur is burned, a minimum niter loss would be about 3 percent, i.e., 3 pounds of 96 percent nitrate of soda per 100 pounds of sulfur burned. In a plant operating at 98 percent yield on sulfur burned, with burner gas containing 10 percent sulfur dioxide, and with all niter losses in the exit gas, the assumed 3 percent niter loss would be equivalent to approximately 0.12 percent nitric oxide (NO) by volume in the exit gas.

The minimum niter losses differ for each plant depending on such factors as rate of operation, design and altitude of the plant, raw material, and total niter in circulation.

Acid Mist — Losses of acid mist and mechanically entrained acid spray in the exit gas vary with the design of the Gay Lussac tower. These losses are usually much less than 0.1 percent of the acid produced.

Other Losses — When high-purity sulfur is the raw material, other losses are small and may consist of nitrogen oxides or sulfur dioxide gases vented from process acid tanks and leakage from equipment. Sulfur losses occur chiefly from windage or washage of sulfur from raw-material storage piles.

### Emissions From the Chamber Process

Composition — The exit gases are composed of nitrogen, oxygen, sulfur dioxide, nitrogen oxides, moisture, acid mist, mechanically entrained acid spray, and sometimes carbon dioxide. The nitrogen dioxide is responsible for the normally reddish-brown color of the exit gases. The components of interest from an air pollution standpoint are sulfur dioxide, nitrogen oxides, and acid mist and spray.

Range of Emissions — In sulfur-burning plants, sulfur dioxide emissions vary normally from less than 0.1 to 0.2 percent by volume. When other raw materials are used, emissions may be twice as high (0.2 to 0.4 percent).

Emissions of oxides of nitrogen vary usually from 0.1 to 0.2 percent or more by volume, expressed as $NO_2$.

Concentrations of acid mist, composed of sulfuric acid and dissolved nitrogen oxides, vary from 0 to about 30 milligrams per standard cubic foot of exit gas.

Since the cooling air temperature for lead chambers is lower in winter than in summer, all of these emissions are usually lowest in winter and highest in summer.

Table A1 presents data from two recent tests of emissions from chamber plants.

Operating Factors Affecting Emissions — Operation in most chamber plants is more an art than a science. Very few control instruments are used. Good operators do not need formal technical training but must have experience on the job.

Emission levels are most affected by the following operating factors:

Concentration of sulfur dioxide in the burner gas.

Concentration of oxygen in the exit gases.

Ratio of nitric oxide to nitrogen dioxide in the gas entering the first Gay Lussac tower.

Maintenance of an adequate amount of niter in circulation; the amount varies with plant design, rate of operation, and ambient temperature.

Temperature and concentration of acid entering the final Gay Lussac tower.

The operator is guided in his adjustments by observations of temperature differences and acid concentration in various parts of the system, color of the gases, manual analyses for oxygen and sulfur dioxide, and amount of acid in circulation.

Methods of Control — Recovery equipment is rarely employed for pollutants in the exit gases from the final Gay Lussac tower. Plant 1 in Table A1 was equipped with a water scrubber after the final Gay Lussac tower. The scrubber reduced the concentrations of sulfur dioxide by about 40 percent and of nitrogen oxides by about 25 percent. This scrubber recirculated the same water; the amount of purge and degree of saturation of sulfur and nitrogen oxides in the scrubber water were unknown. The efficiency of the scrubber in removing acid mist was not determined because of excess carryover of scrubber water in the stack.

Startup and Shutdown Losses — After shutdowns lasting less than 24 hours, starting up presents few problems and results in little increase in normal emissions. Such startups rarely require as much as 6 hours to achieve normal operation.

After shutdowns so long that acid and equipment are cold, 24 hours or more may be required to reach normal emission levels. Higher-than-normal emissions will occur more frequently and for longer periods than in plants shut down for less than 24 hours. Much more time is required to achieve normal conditions in an ore-burning plant than in a sulfur-burning plant.

Other Losses — Loss of solid sulfur by windage and washage during unloading and from outdoor storage piles are appreciable, usually from 1 to 2 percent of the sulfur delivered. Dust settles rapidly and completely within a short distance, however, usually within plant boundaries. When sulfur is purchased in molten form, such losses are eliminated.

When the raw material is sulfide ore, losses similar to those from solid sulfur may occur, but again any dust settles rapidly.

When spent acid is a raw material, or anhydrous ammonia is involved, ammonia, acid gas, and other odors may be detected while materials are pumped to or from tank cars or storage tanks.

There is no appreciable escape of vapor from product acid storage tanks. Because the process equipment is under suction or at very low pressure, emissions from gas leakage are negligible.

### Current and Future Air Pollution Potential

Since the total tonnage of acid made by the chamber process is small and the individual plants are also relatively small, the emissions from these plants represent a low air pollution potential in the United States.

Concentrations of sulfur dioxide in the exit gases are lower in the average chamber plant than in the average contact plant. Exit gases in the chamber plant contain as much or more nitrogen oxides as sulfur dioxide, while stack gases in the contact plant contain essentially no nitrogen oxides. The presence of nitrogen oxide constituents may be readily detected by their highly visible color.

The future air pollution potential of the chamber process is even lower because use of this process is diminishing.

## CONTACT PROCESS *(6, 7)*

### Introduction

There are a number of different types of contact plants, even among those designed by any one of several competitive vendors. The various types of plants are often referred to by the name of the vendor, i.e., the builder or designer. They include Chemical Construction Company (Chemico®), Leonard-Monsanto, and Titlestad. A few sulfuric acid manufacturers also design and build their own plants.

Contact plants may also be classified according to the raw materials used; e.g., high-purity sulfur, low-purity sulfur, ores and smelter gas, spent and sludge acids, and hydrogen sulfide.

The sulfur-burning plants are sometimes called hot-gas purification plants or more rarely raw-gas units. Contact plants that utilize sulfide ores or crude ores are often called metallurgical or cold-gas purification acid plants. If designed primarily for conversion of spent acid to fresh clean acid, they may be called spray-burning or regeneration plants. In this type of plant, the spent acid is sprayed like oil into the combustion chamber. Plants burning hydrogen sulfide may be of the hot-gas purification type or of the true wet-gas type. In the true wet-gas type, sulfur dioxide gas is not dried and the moisture is allowed to pass through the conversion system.

The term sludge plant applies specifically to plants that process acid sludge whose acidity is too low for use in a spray-burning or regeneration process. Although several processes have been developed for using such sludge acid, only one or two plants are known to employ these processes.

Plants using high-purity sulfur account for about 75 percent of all domestic sulfuric acid production.

### Production of Sulfur Dioxide Gas for the Process

If elemental sulfur is the raw material, it is introduced in solid or molten form, usually molten, into a sulfur burner, which may be operated under suction or pressure, usually the latter. Combustion air from the atmosphere, usually predried and often preheated, is supplied to the burner in such proportion as to produce a substantially clean gas containing 8 to 11 percent sulfur dioxide by volume. The gas leaves the burner at temperatures from 1400 to more than 2000°F, depending on the amount of preheat in the air and on the concentration of sulfur dioxide. At higher temperatures, traces of nitrogen oxides may be present.

If hydrogen sulfide or spent acid is the raw material, it is burned in a combustion chamber similar to the typical burner for molten sulfur. In some instances an auxiliary fuel is required. Usually the exit gas from the combustion chamber contains from 7 to 14 percent sulfur dioxide by volume, the balance being chiefly nitrogen, oxygen, and water vapor. Impurities may consist of dust, carbon dioxide, nitrogen oxides, sulfur trioxide, and unburned hydrocarbons. Temperatures vary from 1400 to more than 2000°F.

Many types of equipment are in use for desulfurizing ores and other sulfur-bearing materials, and produce sulfur dioxide at concentrations from 3 to 14 percent by volume. The balance is nitrogen and oxygen. The gas is usually contaminated with widely varying amounts of dust, metallic fumes, water vapor, and gaseous impurities. These contaminants must be removed in the gas-cooling and purification system. The temperature of the process gas stream to the gas-cooling and purification system may vary from 500 to 1500°F.

### Description of the Contact Process

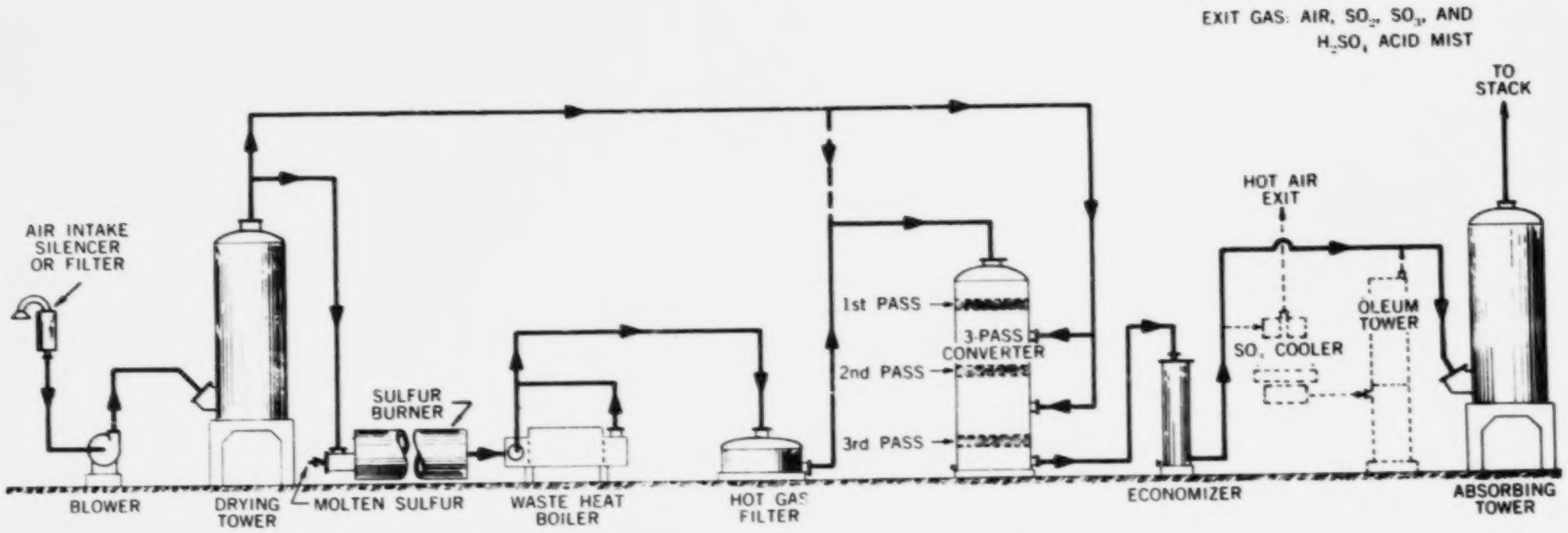
Elemental Sulfur-Burning Plants — Frasch-process or recovered sulfur from oil refineries is melted, settled, or filtered to remove ash, and is pumped continuously into a combustion chamber. The combustion chamber is usually called a sulfur burner or furnace. If the sulfur is received molten, all filtration and most of the settling operation are usually omitted.

As shown in Figure 2, combustion air is usually taken directly from the atmosphere into a blower and discharged to a drying tower with 93 to 99 percent sulfuric acid as a drying agent. The dry air containing about 3 milligrams water per cubic foot goes directly into the sulfur burner. In some plants, the drying tower is located at the suction side of the blower (see Figure 3).

Plants of this type operate at pressures of 2 to 6 psig, depending on design, rate of operation, and cleanliness of equipment. The pressure gradually decreases as the gas passes through the plant until it is substantially atmospheric at the exit stack.

The gas leaving the combustion chamber contains 8 to 11 percent sulfur dioxide by volume. Any hydrocarbons in the sulfur are burned to carbon dioxide and water. The gases from the combustion chamber are cooled in a waste heat boiler to about 760 to 840°F. Part of the cooling may be achieved by injecting cold, dry air into the gas stream. The sulfur dioxide gas from the boiler may be passed through a "hot-gas filter" to remove dust.

The cooled sulfur dioxide gas then enters the solid catalyst converter. The specific inlet gas temperature is dependent upon the quantity and quality of the catalyst and the composition and flow rate of the sulfur dioxide gas.


EXIT GAS: AIR, $SO_2$, $SO_3$, AND
$H_2SO_4$ ACID MIST
TO STACK
AIR INTAKE SILENCER OR FILTER
HOT AIR EXIT
1st PASS
2nd PASS
3rd PASS
3-PASS CONVERTER
$SO_3$ COOLER
OLEUM TOWER
SULFUR BURNER
BLOWER
DRYING TOWER
MOLTEN SULFUR
WASTE HEAT BOILER
HOT GAS FILTER
ECONOMIZER
ABSORBING TOWER

(When four-pass converter is used, cooling after both second and third passes is done by air quench.)

Figure 2 — Gas flow diagram for typical sulfur-burning contact plant in which air quench is used for part of converter interstage cooling.

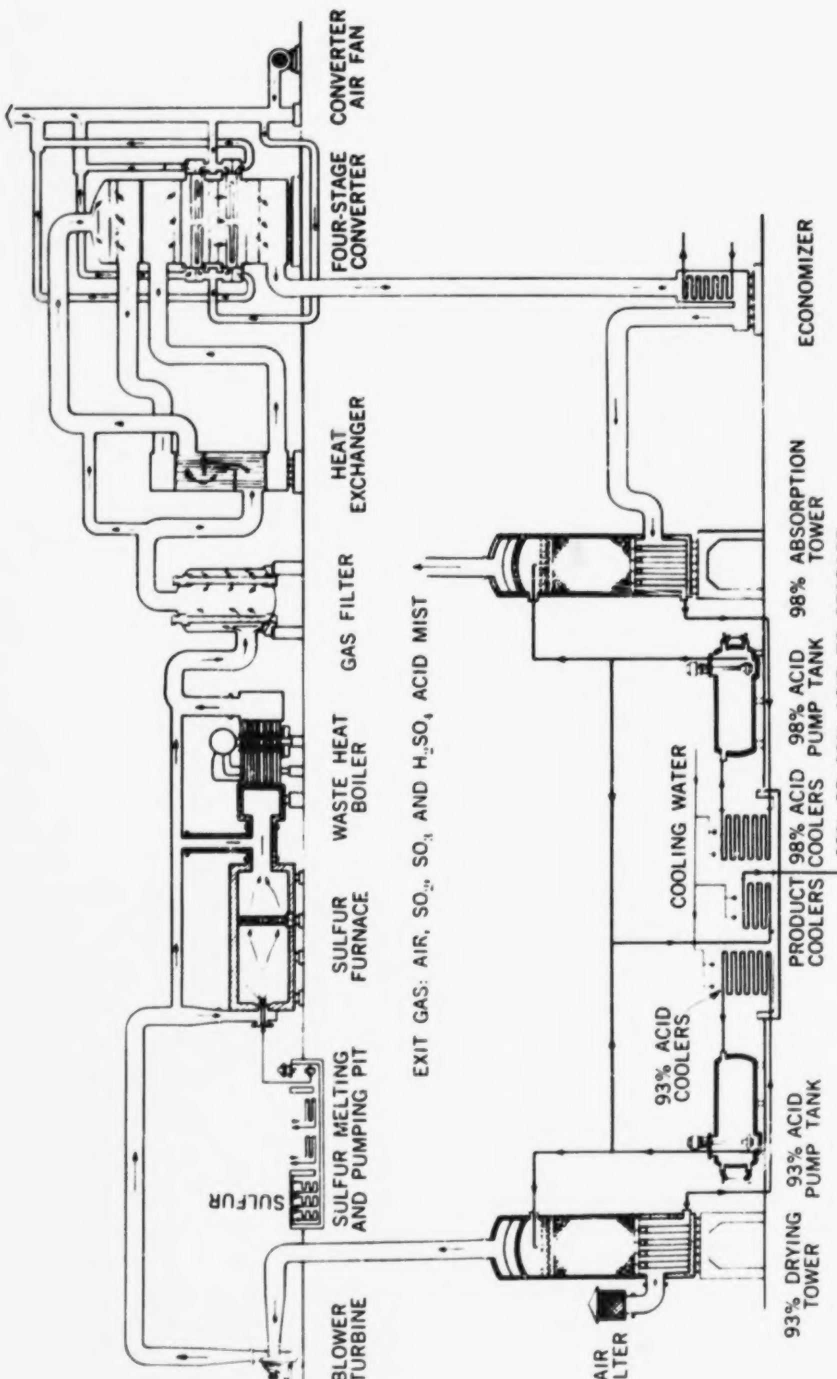

AIR BLOWER AND TURBINE
SULFUR
SULFUR MELTING AND PUMPING PIT
SULFUR FURNACE
WASTE HEAT BOILER
GAS FILTER
AIR FILTER
HEAT EXCHANGER
FOUR-STAGE CONVERTER
CONVERTER AIR FAN
EXIT GAS: AIR, $SO_2$, $SO_3$ AND $H_2SO_4$ ACID MIST
AIR FILTER
93% DRYING TOWER
93% ACID PUMP TANK
93% ACID COOLERS
PRODUCT COOLERS
COOLING WATER
98% ACID COOLERS
98% ACID PUMP TANK
98% ABSORPTION TOWER
93% OR 98% ACID TO STORAGE
ECONOMIZER

Figure 3 — Flow diagram for typical sulfur-burning contact plant in which air quench is not used for converter gas cooling.

The catalyst is usually placed in several horizontal trays or beds in series. Gas cooling is provided between the various stages or passes. There may be one or more catalyst layers in each pass. Converters usually incorporate two, three, or four stages, rarely more than four. In general, the greater the number of catalyst stages, the higher the conversion efficiency of sulfur dioxide to sulfur trioxide. Conversely, the leaner the gas, the fewer the passes required. As shown in Tables A2 and A3, usually from 95 to 98 percent of the sulfur dioxide is converted to sulfur trioxide, with an accompanying large evolution of heat. Maximum conversion cannot be obtained if temperatures in any stage become too high. Therefore, various types of gas coolers are employed between converter stages. Gas cooling may be affected by waste heat boilers, steam superheaters, or tubular heat exchangers. Cooling may also be accomplished by injecting cold, dry air (see Figure 2).

The concentration of sulfur trioxide leaving the converter is approximately the same as that of the entering sulfur dioxide. The concentration of sulfur trioxide is lower, however, if interstage cooling has been effected by injecting cold air (called air quench or air dilution). The converter discharge gas is normally within a temperature range of 800 to 850°F. In addition to the usual 8 to 11 percent sulfur trioxide, the exit gas contains oxygen, nitrogen, unconverted sulfur dioxide, and traces of moisture and carbon dioxide. The moisture results from incomplete drying of combustion air or from burning of hydrocarbons in the sulfur. Trace amounts of carbon dioxide are also introduced from the hydrocarbon combustion.

The converter exit gas is cooled to between 450 and 500°F in an economizer supplementing a boiler feedwater heater or a tubular heat exchanger, which may simultaneously preheat the combustion air to the sulfur burner. Further cooling may take place in tubular heat exchangers or in the gas duct before the gas enters the absorber. The extent of cooling depends largely on plant design and whether or not oleum is to be produced. The cooled gas stream enters the absorption tower, where the sulfur trioxide is absorbed countercurrently in a circulating stream of 98 to 99 percent sulfuric acid. The sulfur trioxide combines with the water in the acid and forms more sulfuric acid. In the absorption tower, the sulfur trioxide is normally absorbed with an efficiency of substantially 100 percent. Any unabsorbed sulfur trioxide passes to atmosphere. In some plants the absorber is equipped with a mist eliminator for removal of acid mist and spray in the exit gas stream.

If oleum is produced, the sulfur trioxide passes through an oleum tower before going to the 98 percent absorption tower. The oleum is fed with acid from the 98 percent absorption system. The sulfur trioxide gas is cooled to a much lower temperature before entering the oleum tower than would occur if only 98 percent acid were to be produced. The oleum tower is unable to absorb all of the sulfur trioxide. Therefore the effluent gas from the oleum tower is passed through the 98 percent absorber for recovery of residual sulfur trioxide.

The recirculating acid in the 98 percent absorber and the oleum tower, or towers, if operating, increases in temperature as a result of (1) sensible heat from the sulfur trioxide stream, (2) exothermic heat from the reaction of sulfur trioxide and water, and (3) heat of solution of sulfur trioxide in oleum. Thus, many acid coolers are required to keep the acid at the desired temperature for efficient absorption of sulfur trioxide. Acid usually enters the 98 percent absorption tower between 150 and 190°F and at a concentration of 98.6 to 99 percent. The exact temperature and concentration are those that result in the lowest visibility for the exit gases.

The drying tower, which removes moisture from the combustion air, is supplied with acid from the 98 percent absorber and is similar in construction. The recirculating acid in the drying tower is maintained within a range of 93.2 percent (66° Bé) to 99 percent. The acid must be cooled because of the heat evolved by dilution of the acid with moisture from the combustion air. The increased volume of acid in the drying tower resulting from this dilution is returned to the 98 percent absorber or pumped to storage.

A few contact plants, regardless of raw material used, produce 100 percent sulfur trioxide vapor or liquid as part of their product. This product is most easily made, however, in sulfur-burning units. The 100 percent sulfur trioxide is frequently used to fortify lower concentrations of oleum to the 65 percent grade. Oleum concentrations stronger than approximately 40 percent cannot be made in contact plants without auxiliary equipment to produce 100 percent sulfur trioxide.

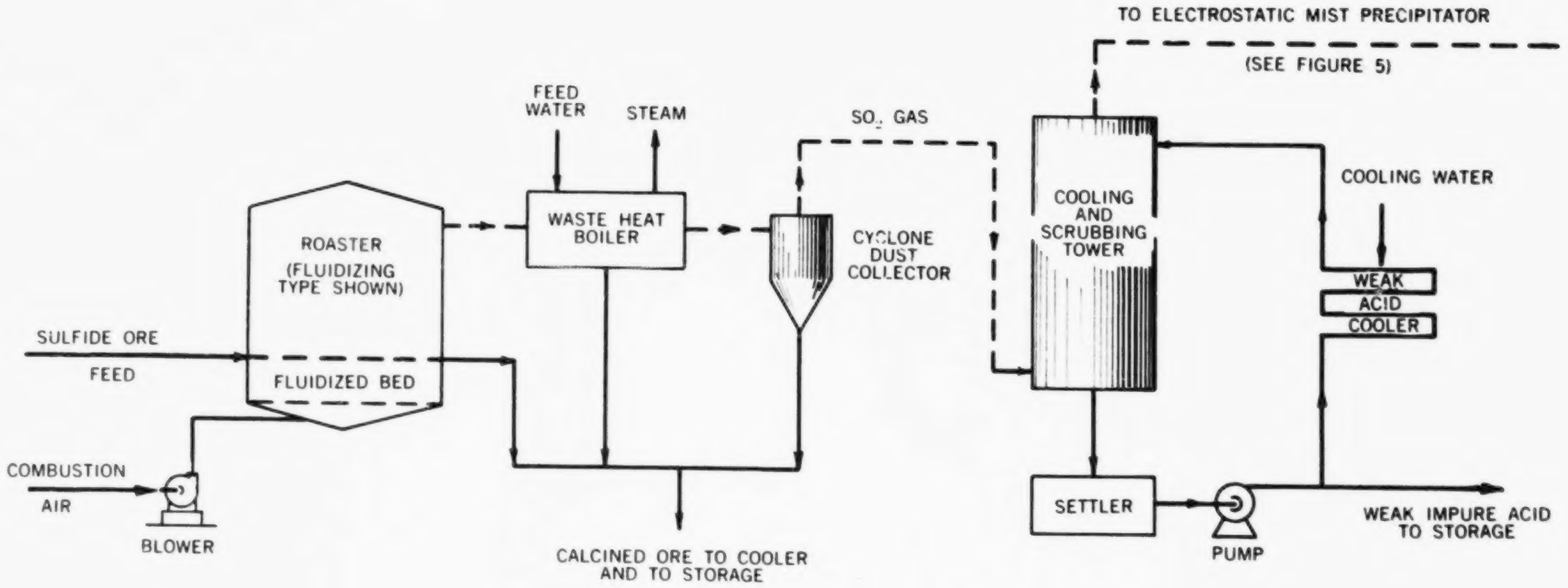
Only one plant in the United States presently operates with crude sulfur ores (15 to 25 percent S) as the raw material. It is identical to plants using sulfide ores.

Sulfide Ores and Smelter Gas Plants — The metallurgical-type contact plant is more elaborate and expensive than the sulfur-burning plant. It may cost 3 times as much as the sulfur-burning plant, with lower yields and higher operating costs. When the price of sulfide ore or smelter gas is low compared to sulfur, however, sulfuric acid may be produced at a lower cost. These metallurgical plants account for about 15 percent of total sulfuric acid production in the United States.

Sulfur dioxide gas from smelters is available from such equipment as copper converters, reverberatory furnaces, roasters, and flash smelters. The sulfur dioxide concentrations and temperatures of these gases are often highly variable. When pyrites or zinc concentrates are the raw material, they are roasted in special furnaces or roasters with undried atmospheric air. The effluent gas stream usually contains 7 to 14 percent sulfur dioxide and rarely exceeds 1400°F. Sintering machines, which are used infrequently, produce a gas that seldom contains more than 6 percent sulfur dioxide.

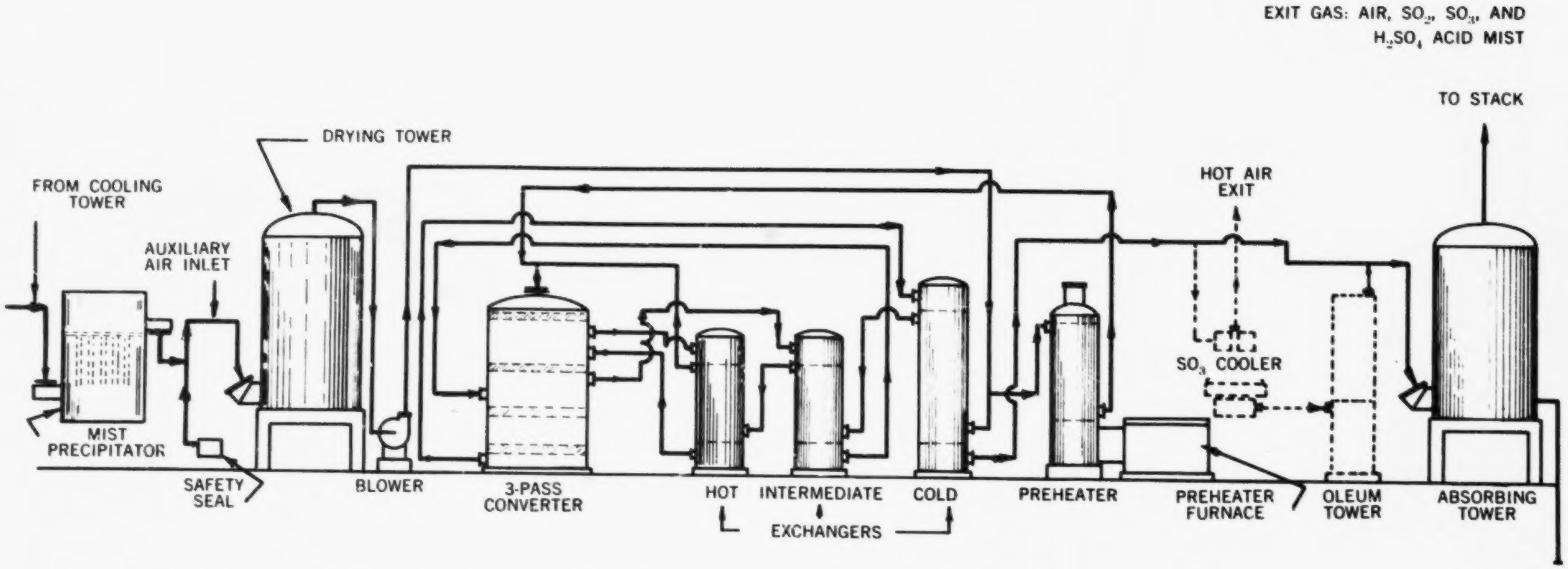
The sulfur dioxide is contaminated with dust, acid mist, and gaseous impurities, which must be removed if high-quality acid is to be produced. To remove the impurities, along with excessive amounts of water vapor, the gases must be cooled to essentially atmospheric temperature. Purification equipment consists of cyclone dust collectors, electrostatic dust and mist precipitators, and scrubbing and gas-cooling towers in various combinations as shown in Figure 4.

After the gases are adequately cleaned and the excess water vapor removed, they are countercurrently scrubbed with 66° Bé acid in a drying tower. The sulfuric acid removes substantially all of the remaining water vapor before the gases pass to the blower (see Figure 5). Since the plant is under suction up to this point, no gas leakage can occur.


TO ELECTROSTATIC MIST PRECIPITATOR
(SEE FIGURE 5)
FEED WATER
STEAM
$SO_2$ GAS
ROASTER (FLUIDIZING TYPE SHOWN)
WASTE HEAT BOILER
CYCLONE DUST COLLECTOR
COOLING AND SCRUBBING TOWER
COOLING WATER
WEAK ACID COOLER
SULFIDE ORE FEED
FLUIDIZED BED
COMBUSTION AIR
BLOWER
CALCINED ORE TO COOLER AND TO STORAGE
SETTLER
PUMP
WEAK IMPURE ACID TO STORAGE

$SO_2$ gas shown as dotted lines. Cyclone dust collector may be replaced or supplemented byelectrostatic dust precipitator.

Figure 4 — Flow diagram for typical metallurgical-type contact plant (roasting and gas purification equipment).


EXIT GAS: AIR, $SO_2$, $SO_3$, AND
$H_2SO_4$ ACID MIST
TO STACK
HOT AIR EXIT
DRYING TOWER
FROM COOLING TOWER
AUXILIARY AIR INLET
$SO_3$ COOLER
MIST PRECIPITATOR
SAFETY SEAL
BLOWER
3-PASS CONVERTER
HOT
INTERMEDIATE
COLD
EXCHANGERS
PREHEATER
PREHEATER FURNACE
OLEUM TOWER
ABSORBING TOWER

See Fig. 4 for roasters and equipment ahead of mist precipitator.

Figure 5 — Flow diagram for typical metallurgical type contact plant (drying, conversion, and absorption equipment).

Beginning with the drying tower, the ore and smelter gas plants are very similar to sulfur-burning plants, but these units usually have no sulfur-burning facilities, waste heat boilers, superheaters, or economizers after the boiler. The only waste heat boiler, if any, is located after the sulfur dioxide producing equipment to provide initial cooling of the hot, dirty gases.

The cool, clean sulfur dioxide gas stream is heated to about 800°F before it enters the converter. The heat is supplied in tubular heat exchangers by passing the cold sulfur dioxide gas stream countercurrent to the hot sulfur trioxide gas from the catalyst converters. The sulfur trioxide gas is thereby cooled to a suitable temperature for absorption in the final absorber tower.

Spent-Acid and Hydrogen Sulfide Burning Plants — Plants that burn spent acid and hydrogen sulfide are similar to plants processing ores and smelter gas but are simpler and less expensive. However, plants for spent acid are more expensive than sulfur-burning units.

Spent acid and/or hydrogen sulfide are introduced into the combustion chamber and burned with undried atmospheric air. If only spent acid is burned, auxiliary fuel may be required. A common procedure for spent-acid plants is to burn simultaneously hydrogen sulfide, spent alkylation acid, and sulfur. The effluent combustion gas rarely contains more than 14 percent sulfur dioxide, but temperatures may be as high as 2400°F. Spent-acid plants produce higher concentrations of nitrogen oxides and carbon dioxide in the sulfur dioxide gas stream than are encountered in contact plants using high-purity sulfur.

Two types of plants are used. In one the sulfur dioxide and other combustion products are passed through gas-cooling and mist-removal equipment before entering the drying tower. Gas cooling is effected by a waste heat boiler followed by various types of gas coolers. Mist removal is accomplished usually by electrostatic precipitators. Concentrated sulfuric acid removes moisture from the sulfur dioxide and air stream passing through the drying tower. A blower draws the gas from the drying tower and discharges the sulfur dioxide gas to the sulfur trioxide converter. The balance of this process is essentially the same as that in the previously discussed ore-roasting process.

In a few "wet-gas plants" the above-described process is much simplified. The wet gases from the combustion chamber and waste heat boiler are charged directly to the converter with no intermediate treatment. The gas from the converter then flows to the absorber, through which 60 to 66° Bé sulfuric acid is circulating. In this type of plant, the absorber is not highly efficient because the sulfur trioxide is in the form of sulfuric acid mist because of the excessive moisture content of the gases. Highly efficient mist recovery equipment after the absorber is essential. Wet gas plants are used primarily for hydrogen sulfide or hydrogen sulfide plus elemental sulfur.

Catalysts — Catalysts of the vanadium pentoxide type are used almost exclusively in contact plants throughout the United States. Catalyst containing platinum is seldom used because of its susceptibility to poisoning by trace amounts of foreign elements. The vanadium catalysts consist mainly of vanadium pentoxide along with various promoters deposited usually on a highly porous siliceous carrier. The catalyst may be in extruded, pelleted, or tableted form. The individual pellets are usually cylinders of about 1/4- to 1/2-inch diameter. The pellets may also be similar in shape to aspirin tablets.

A vanadium pentoxide catalyst, if well treated, has an indefinitely long life, with no appreciable drop in activity. In practice, the sulfur dioxide gas stream is seldom completely clean and operating temperatures may occasionally rise too high. These factors can result in a slight reduction of catalyst activity. The first catalyst stage is normally the only one in which the activity of the catalyst is appreciably affected.

The normal impurities carried into the catalyst are dust from the raw materials,. scale from converter equipment, and iron sulfate resulting from corrosion of equipment ahead of the catalyst. Although the impurities do not initially affect activity of the catalyst appreciably, the voids around the catalyst become filled, with a resulting increase in pressure drop. Many sulfur-burning plants rescreen the top or first layer of catalyst each year to reduce the pressure drop. In metallurgical plants the necessity for rescreening occurs less often. Most sulfur-burning plants schedule an annual shutdown for boiler inspection, during which time all accumulated maintenance work, including catalyst rescreening, is completed.

The catalyst in the first stage gradually loses activity as the catalyst pores become partially filled with dust. Not all of the dust can be removed by rescreening. When the catalyst activity has decreased enough to affect the over-all yield appreciably, part of the first stage catalyst is normally replaced with new catalyst. The expense for replacement of affected catalyst is not a serious item over a period of years.

**Emissions From the Contact Process**

Composition — The major source of emissions from contact sulfuric acid plants is waste gas from the absorber exit stack. The discharge gas to atmosphere contains predominantly nitrogen and oxygen but also contains unreacted sulfur dioxide, unabsorbed sulfur trioxide, and sulfuric acid mist and spray. When the waste gas reaches the atmosphere, sulfur trioxide is converted to acid mist. Trace amounts of nitrogen oxides may also be present, e.g., when a feed containing nitrogenous matter is used. Minor additional quantities of sulfur dioxide and sulfur trioxide may come from storage tank vents, from tank truck and tank car vents during loading operations, from sulfuric acid concentrators, and from leaks in process equipment.

Loss of Unconverted Sulfur Dioxide — The major emission from a contact plant is sulfur dioxide from the absorber exit stack. Sulfur dioxide in the stack gas results from the incomplete conversion of sulfur dioxide to sulfur trioxide in the catalyst converter. Conversion efficiency of 98.0 to 98.5 percent is attainable with proper plant design. Higher conversion efficiencies require a more expensive plant and result in higher production costs.

Most contact plants are purchased from vendors who normally guarantee a conversion efficiency of 96 to 98 percent. Guarantees of lower or higher efficiencies are infrequent today. Although the guarantees are usually based on plant operation at not more than rated capacity, the vendor often builds in extra capacity to insure his guaranteed conversion efficiency. Thus, some plants may operate at capacities appreciably greater than rated capacity and still meet the vendor's guaranteed conversion efficiency.

In Germany a contact plant process has been offered recently that claims to reduce the concentration of $SO_2$ in the gases leaving the converter system to 0.03 percent sulfur dioxide(*8*). The process consists of the addition to the system of a sulfur trioxide absorbing tower just ahead of the final stage of conversion. Removal of sulfur trioxide at this point results in a reported over-all conversion efficiency of 99.7 percent. It is claimed that plants utilizing this design can be built for approximately the same investment as plants of commercial design in Germany and that production costs are also equal. Information is not available at this time with which to compare investment and operating costs in this country.

In many existing sulfur-burning contact plants or in any newly designed sulfur-burning contact plants it is possible to reduce sulfur dioxide in the exit gas to 0.1 percent by operating with very dilute gas. Operation in this manner increases acid manufacturing costs.

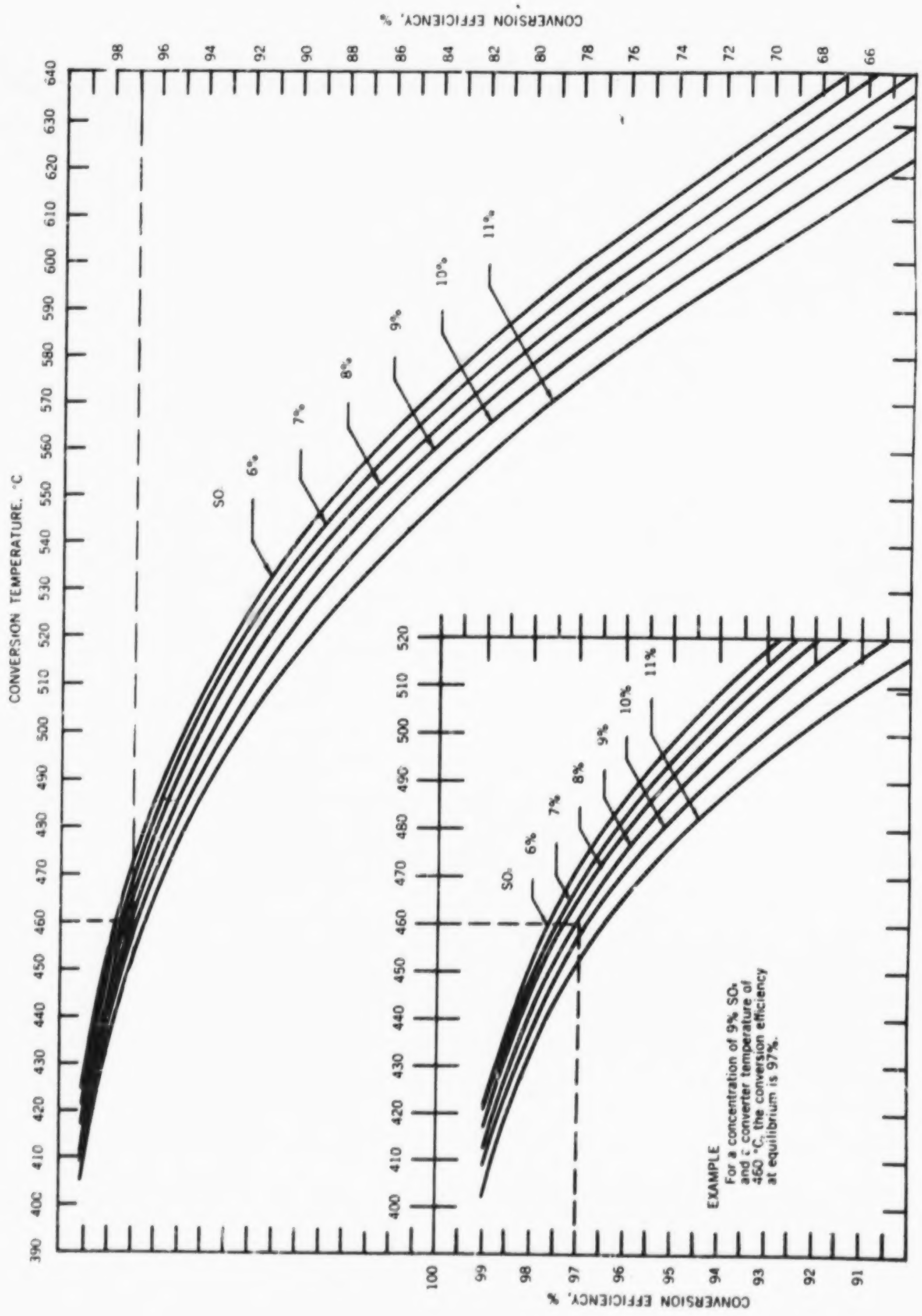
Figure 6 shows the equilibrium efficiencies at various temperatures with commonly used gas compositions derived from burning elemental sulfur(*9*). The values in Figure 6 do not apply to other gas compositions, such as would be obtained from other raw materials. The "percent $SO_2$" is the volume composition entering the converter except for plants of the air dilution type. In such plants the "percent $SO_2$" is the "equivalent percent $SO_2$", i.e. the percent sulfur dioxide that would have entered the converter if all air dilution had taken place ahead of the converter rather than at various points in it.

The test data in Tables A2 and A3 show an efficiency range of 95.6 to 98.5 percent conversion of sulfur dioxide to sulfur trioxide. The mean conversion efficiency for the 31 tests at typical contact plants is 97.3 percent. It should be noted that the conversion efficiency figure usually includes any loss of sulfur dioxide absorbed in the drying tower, i.e. in plants where the drying tower dries wet sulfur dioxide rather than air. This occurs because of the usual location of sampling points when determining conversion efficiency.

The unconverted sulfur dioxide from the catalyst converter passes through the absorption system and is discharged to the atmosphere. Tables A2 and A3 show that sulfur dioxide concentrations in the absorber discharge stack gas range from 0.13 to 0.54 percent. The mean for the 33 tests is 0.26 percent sulfur dioxide.

Figure 7 shows the percent conversion of sulfur dioxide to sulfur trioxide versus percent sulfur dioxide in exit gas for all plants listed in Tables A2 and A3. Reduction of sulfur dioxide in the exit gas is seen as a direct function of increased sulfur dioxide conversion. The conversion efficiency and the concentrations of sulfur dioxide in the exit gas also depend upon the concentration of sulfur dioxide and oxygen in the gas entering the converter. Figure 8 shows the relationship for sulfur burning plants in which no air quench is used(*10*). Figure 9 applies to sulfur burning plants of air dilution type and shows the conversion corresponding to the sulfur dioxide and oxygen content of the exit gas(*11*). In this case, no test is required for the gas entering the conversion system. Figure 10 shows sulfur dioxide emissions for various conversion efficiencies for sulfur dioxide.

Stack Gas Losses of Acid Mist and Spray — Acid-mist content of gas leaving the absorber is shown in Tables A2 and A3. Data collected in 33 tests show that acid-mist and spray content varied from 1.1 to 48.8 milligrams per standard cubic foot of stack gas. The average of these values is 12.9 milligrams; (one value from a "wet gas" plant burning hydrogen sulfide is omitted from this average because it concerns an unusual process that is not comparable with the operations of other plants included in the tabulation).



EXAMPLE
For a concentration of 9% $SO_2$
and a converter temperature of
460 °C, the conversion efficiency
at equilibrium is 97%.

Figure 6 — Equilibrium conversion efficiencies at various temperatures and gas compositions.

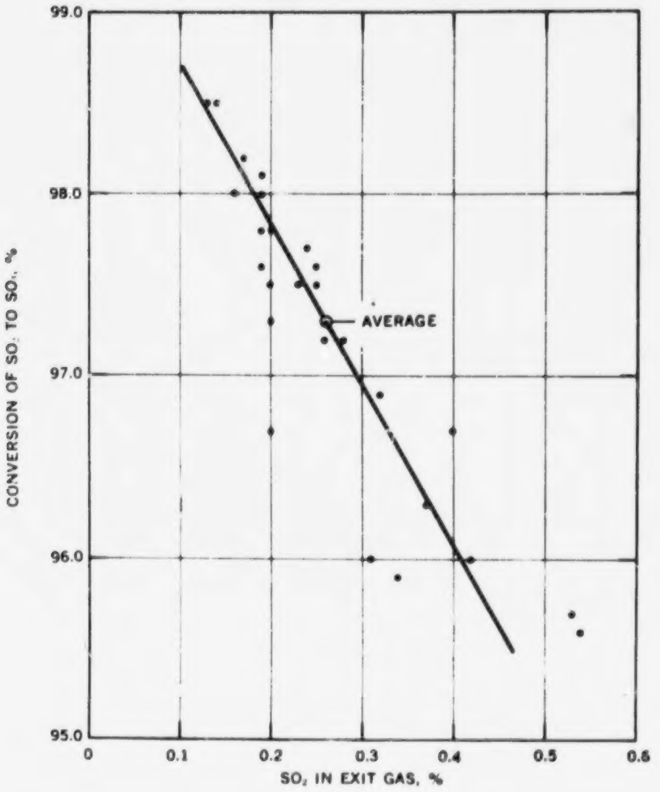


**Figure 7** — Relationship of conversion effiicency to $SO_2$ in exit gas (based on data in Tables A2 and A3).

Auxiliary recovery equipment will reduce the content of acid mist and spray in the absorber gas as shown in Table A3. In 14 tests conducted in 10 plants under various conditions, the acid-mist and spray content of the absorber gas was reduced to values ranging from 0.18 to 23.4 milligrams per cubic foot, with an average at 3.7 milligrams. Stack impingement may reduce the acid content of the gases even more before they are exhausted to the atmosphere.

Table A3 illustrates the effectiveness of three different types of mist and spray recovery equipment, including electrostatic precipitators, glass-fiber filters, and wire-mesh filters. When designed for high performance, glass-fiber eliminators and electrostatic precipitators show a high degree of recovery. Two tests with alloy wire-mesh eliminators (plants 2A and 2B, Table A3) show good recovery when the acid is present predominantly as particles larger than 3 microns diameter, but substantially lower recovery when the proportion of small particles is greater.

Internal spray eliminators (spray catchers) are installed in the top sections of many absorbers to aid in the removal of large acid particles entrained in the exit gas. In most cases, the spray eliminators do an effective job of removing entrained acid spray and part of the mist.

Spray and mist may also be formed in the exit stack when gas cooling and velocity are excessive; however, spray is rarely a problem in the exit gas of a stack of adequate diameter. The white plume may often be acid and mist that was in the gas leaving the absorber.

Stack Gas Losses of Unabsorbed Sulfur Trioxide — Unabsorbed sulfur trioxide is discharged to the atmosphere from the absorber exit stack. The sulfur trioxide in the exit gas is hydrated to sulfuric acid from contacting atmospheric moisture and forms a visible white plume of acid mist.

Because the sampling and analytical techniques for sulfur trioxide are more complex than for sulfur dioxide and sulfuric acid mist, test data for unabsorbed sulfur trioxide are more limited. The test results for sulfur trioxide may be slightly low because of the possibility of partial absorption of sulfur trioxide in the acid-mist filter of the sample train. The test results for plant 5A, Table A3, show the same concentration of sulfur trioxide, 1 to 2 milligrams per cubic foot, entering and leaving the glass-fiber mist eliminator. The amount of sulfur trioxide absorption in an acid-mist filter would not, therefore, appear to be appreciable.

The reported values for unabsorbed sulfur trioxide vary from less than 0.5 milligram per cubic foot for plant 19 to 48 milligrams per cubic foot for plant 16, Table A2. On the basis of sulfur trioxide conversion to acid mist in the atmosphere, the 48 milligrams per cubic foot would account for 85 percent of the total acid-mist emission for plant 16, Table A2. Likewise, the less than 0.5 milligram per cubic foot would be equivalent to less than 7 percent of the total acid mist for plant 19, Table A2. Although the concentrations for unabsorbed sulfur trioxide can vary considerably, they can comprise an appreciable part of the total acid-mist emission, usually under upset operating conditions.

If the absorber discharge stack shows essentially no visible plume, the operator can assume that loss of unabsorbed sulfur trioxide is neglible. If a

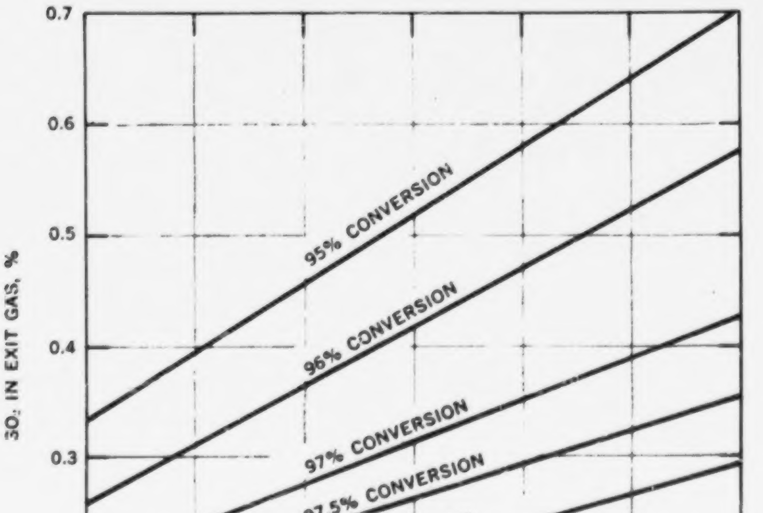


Figure 8 — Percent conversion of sulfur dioxide to sulfur trioxide for plants with no air dilution(*10*).

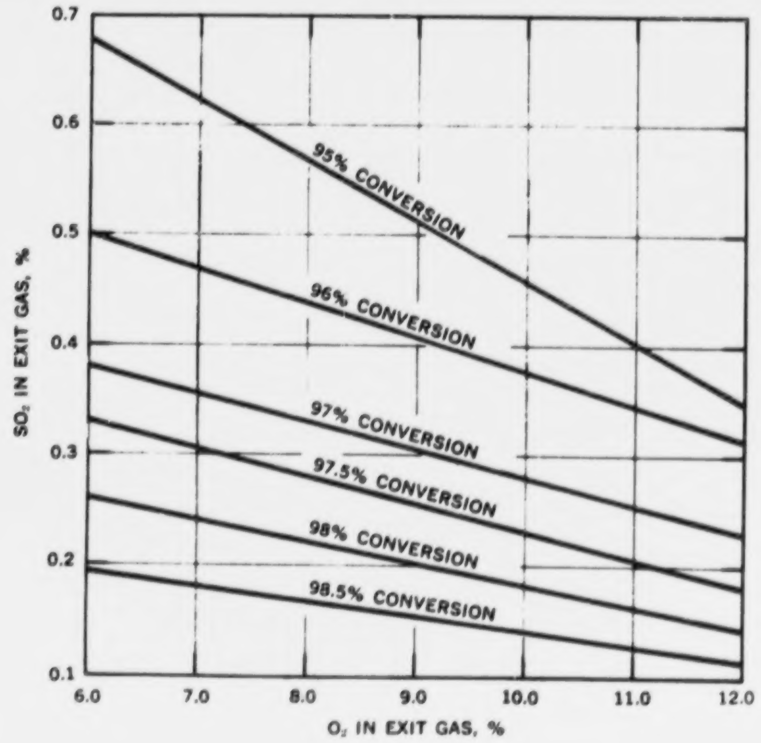


Figure 9 — Percent conversion of sulfur dioxide to sulfur trioxide for plants with air dilution(*11*).

detached plume is observed from the absorber discharge stack, then most of the acid-mist emission could be accounted for by unabsorbed sulfur trioxide.

Formation of Sulfuric Acid Mist — Water-based acid mists are formed as a result of the presence of water vapor in the process gases fed to the converter. The drying towers in most contact plants are able to dry the air or sulfur dioxide gas to a moisture content of about 3 milligrams per standard cubic foot. The remaining moisture combines with the sulfur trioxide after the converter, when the temperature falls below the dew point of sulfur trioxide. The acid mist so formed is very difficult to remove in the absorber. Much of it passes through the absorber to the atmosphere.

Theoretically, the 3 milligrams of water vapor will form approximately 15 milligrams of sulfuric acid. In a sulfur-burning plant producing 100 tons per day sulfuric acid with 9 percent sulfur dioxide gas at 96 percent conversion efficiency, the gas volume leaving the drying tower is about 5700 standard cubic feet per minute. If all of the acid mist formed from the moisture in the dried air were lost in the absorber exit gas, it would amount to 271 pounds of acid per day. Part of the mist is probably removed in the absorber, however.

In one rare type of plant, the wet gas plant, no attempt is made to remove water vapor either from the combustion air or from the gas resulting from combustion of the hydrogen sulfide. Hence, the amount of water vapor in the gas entering the converter is more than enough to combine with all of the sulfur trioxide produced. As a result, the entire output of the plant initially is in the form of acid mist rather than sulfur trioxide as in all other types of plants. In such a plant, if operated with 7 percent sulfur dioxide gas entering the converter and at 96 percent conversion efficiency, the gas leaving the converter, after cooling, would contain approximately 8500 milligrams $H_2SO_4$ mist per standard cubic foot. Actually, some of the mist is recovered in the gas-cooling equipment and the balance in high-efficiency recovery equipment. Plant 7, Table A3 illustrates this case. After cooling, the gas still contained 2533 milligrams acid mist. The glass-fiber eliminator reduced this total to 2.3 milligrams in the stack gas, equivalent to 99.99 percent collection efficiency.

In sulfur-burning plants, mists may also be formed from water resulting from the combustion of hydrocarbon impurities in the sulfur. For example, a 100-ton acid plant at 96 percent yield would burn approximately 68,200 pounds per day of sulfur. If 0.1 percent of the sulfur were organic matter containing 20 percent hydrogen, all of which formed water and then acid mist, 667 pounds per day of sulfuric acid mist would be formed from this source. The 667 pounds of mist from combustion of organic matter is more than double the 271 pounds formed from moisture in the air leaving the drying tower. Dark sulfur may contain up to 0.5 percent organic matter. Thus, in a sulfur-burning plant, appreciably more mist may be formed from combustion of organic matter in sulfur than from moisture in the dried air.

In plants other than those burning high-purity sulfur, if trace amounts of hydrocarbon are present in the cold gas purification system, they are substantially scrubbed out in the drying tower. In plants of these types, most of the acid mist is formed from trace amounts of moisture leaving the drying tower and from moisture formed by combustion of trace hydrocarbons.

Even with no moisture present in the inlet gases, however, it is possible

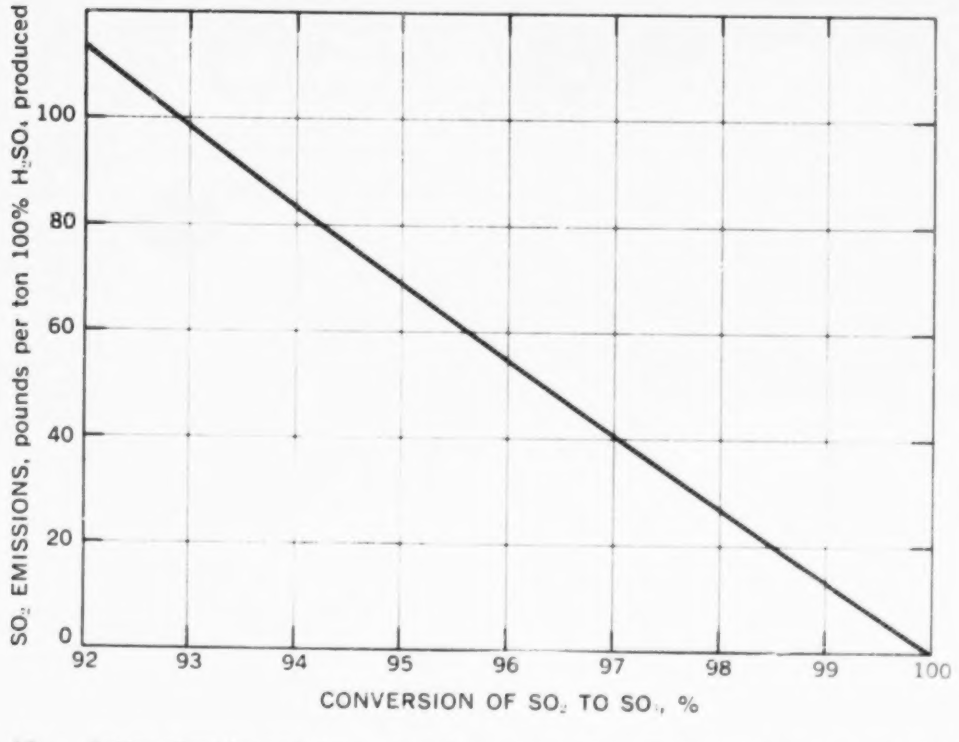


Figure 10 — Sulfur dioxide emissions at various conversion efficiencies (per ton of equivalent 100% $H_2SO_4$ produced)

to form in the absorbing tower very fine acid mist from shock cooling of the inlet gases or from excessive gas velocity.

Small amounts of nitrogen oxides in the inlet gas to the absorber interfere with the absorption of sulfur trioxide and hence cause visible acid mist in the absorber exit gases. Nitrogen oxides are formed mainly from burning nitrogenous matter in the spent acid or hydrogen sulfide raw materials. Brink(*12*) found that the sulfuric acid collected in a fiber-glass mist eliminator in one typical hydrogen sulfide spent acid plant contained 2 to 5 percent oxides of nitrogen, calculated as nitric acid. Electrostatic precipitators used for mist removal in cold gas purification units may form nitrogen oxides if arcing occurs. Excessive sulfur burner temperature also results in formation of a small amount of nitrogen oxides.

Other than plants that use raw materials containing nitrogenous matter, the oleum-producing plants have the greatest difficulty with visible mist in the exit gas. The amount of the mist appears to be proportional to the percent of plant output in the form of oleum and to the strength of the oleum produced (see Table 6). Plant design and the method and extent of cooling of the sulfur trioxide gases ahead of the oleum tower greatly influence particle size of the acid mist and hence visibility of the exit gases. These variables are not clearly understood.

Comparison of acid-mist concentrations for plants 2A and 2B (Table A2) and plants 5A and 5B (Table A3) show appreciably higher acid-mist concentrations for oleum production than when the same unit was making only 97 percent acid. This agrees essentially with Monsanto's published data (see Table 6). Some of the acid-mist concentrations for plants making oleum, i.e., plants 7A, 7B, and 7C (Table A2), are in the same range as plant 8 (Table A2), which operated with no oleum production. All of these plants operated with very pure recovered sulfur. In many cases where tests were conducted in different plants, other variables such as design, moisture content of dried air, absorber packing and absorbing acid temperature, concentration, circulation, and distribution could also appreciably affect acid-mist emissions. Unfortunately, all pertinent information is not always available.

The acid-mist emission from plant 12 (Table A2), which burns dark sulfur is much higher than that for any of the plants using molten recovered sulfur. This would be expected because of the higher hydrocarbon content of the dark sulfur. Again, however, emissions from plants burning dark sulfur (i.e., plant 11, Table A2) can be as low as those from plants using bright sulfur, or lower. The above-described unknown variables could account for the relatively low emissions from some of the plants burning dark sulfur.

No appreciable difference in ranges of acid-mist concentrations are apparent for the different types of contact sulfuric acid plants. Whether a plant is of sulfur-burning type with or without air dilution, or is of metallurgical or spent acid type does not appear to be significant in regard to acid-mist concentrations in stack gas from an absorber.

The weight percent of acid-mist particles leaving the absorber ahead of any mist-recovery equipment and having a particle size of 3 microns or less ranged from 7.5 to 95 percent of the acid mist for those plants in which particle size was determined. The mean weight percent of such acid mist having a particle size of 3 micron or less for these acid plants is 63.5.

Plants 2A and 2B (Table A2) well illustrate the effect of making oleum. When no oleum was made, only 9.5 percent of the mist particles were less than 3 microns; when oleum was made, 54 percent were less than 3 microns. Any exceptions in other tabulated plants were from causes such as moisture leaks, not related to grade of acid produced.

The visibility of acid mist depends more on particle size than on mist concentration. Thus, a high percentage of particles 3 microns or less in the acid mist usually causes a heavy plume from the absorber stack. Acid mist composed of particles up to about 10 microns is visible in tail gas to a trained observer if present in amounts greater than about 1 milligram of sulfuric acid per cubic foot of gas(6). Conversely, exit gas containing 5 milligrams or more of acid mist per cubic foot may be invisible if the particles are large.

Shutdown and Startup Losses — In plants that produce sulfur dioxide by roasting ores in multiple-hearth roasters, rotary kilns, copper converters, or sintering machines, sulfur dioxide losses will occur with a sudden shutdown. In most cases these losses are minor and exist for a short period of time. In other types of plants, where the sulfur dioxide producing equipment is vapor tight, no escape of acidic gases may be expected.

In startup of a plant that has been shut down for a short period of time and where operating temperatures for the catalyst chamber and the absorbers are maintained, emissions of sulfur oxide may be expected to be in the same range as during normal operations. Depending on climate, size of plant, and quality of insulation, shutdowns may vary from 8 hours in a small plant to 24 hours in a large plant without excessive cooling of the catalyst chamber or other equipment.

When the plant has been offstream long enough to allow the catalyst chamber to cool, it is necessary to preheat the catalyst to its ignition temperature before feeding any sulfur dioxide gas. This preheating is done by use of a fuel, usually oil or gas. In sulfur-burning plants this fuel is burned, instead of sulfur, in the sulfur burner. In plants of metallurgical type, a special auxiliary tubular preheater with a fuel combustion chamber is installed to heat the incoming air indirectly. While the catalyst is being preheated, the sulfur dioxide producing equipment is heated simultaneously.

When the absorber temperature is below about 150°F, absorption efficiency is decreased and the emission of sulfur trioxide and acid mist is considerably above normal. No auxiliary equipment is usually available to preheat the absorbing acid. Preheating with moist atmospheric air or combustion gases is not considered a desirable operating procedure because the moisture present in these gases will dilute the absorber acid, thus reducing absorption efficiency, and may cause corrosion in other parts of the plant. The usual practice in heating absorbing acid is to use the hot sulfur trioxide gas produced in the catalyst chamber. About an hour is usually sufficient to warm the absorbing acid to normal operating temperatures.

Losses of sulfur dioxide and acid mist may be excessive during startup after a long shutdown if, in the haste to resume operation, the vital process equipment has not been preheated sufficiently. The duration of the excessive losses depends primarily on how much the equipment is below normal operating temperatures. It may vary from a few minutes to 12 to 18 hours, depending on temperatures and skill of operation in making necessary adjustments of valves, etc. During this period the emissions to the atmosphere gradually decrease.

Losses From Sulfuric Acid Concentrators — Concentrators are occasionally employed by both producers and users of sulfuric acid. Their function is to concentrate acid that has been produced in a dilute form or acid that has been diluted through use. Concentration may be necessary for reuse or to reduce shipping costs. Use of concentrated acid may make it possible to avoid discharging waste acid into a water course.

Concentration is often accompanied by the evolution of acid mist and sulfur dioxide. The concentrating process is further complicated by the high boiling point of the acid, its corrosiveness, and its tendency to foam when impurities are present.

The two main types of concentrators used in the United States are the vacuum and the drum types. The vacuum type operates under high vacuum with heat applied indirectly. Hence, the boiling point of the acid is much reduced and the acid-mist emissions, if any, are minor. In the drum type, heat is applied directly in the form of hot combustion gases. Emissions of sulfuric acid mist to the atmosphere can be prevented by use of electrostatic precipitators, venturi scrubbers, or glass-fiber eliminators.

Acid-mist emissions taken ahead of the mist-recovery equipment for a drum concentrator are given in Table 4.

TABLE 4. EMISSIONS FROM ACID DRUM CONCENTRATOR

| | | | |
|---|---|---|---|
| Operating rate, % of capacity | 55 | 73 | 100 |
| $H_2SO_4$ concentration rate, tons/day | 82 | 110 | 150 |
| Acid mist emission, mg/scf | 199.2 | 68.0 | 66.1 |
| Particle size, (3 microns and less), wt % | 85 | 86 | 57[a] |

[a] At maximum capacity more entrained large particles are present.

Other Losses — Loss of solid sulfur during unloading of deliveries and from outdoor storage piles by windage and washage are appreciable, usually from 1 to 2 percent of the sulfur delivered. Any dust settles rapidly within a short distance; however, when sulfur is purchased in molten form, all such losses are eliminated. When the raw material is sulfide ore, there may be similar losses.

When spent or sludge acids are raw materials, malodorous gases may escape during unloading or from storage tanks. The quantity is usually small.

Most of the process equipment in a contact plant is under low pressure. Because of the obnoxious odor, any leakage of sulfur dioxide or sulfur trioxide from process equipment is very noticeable. Also sulfur trioxide leaks can be seen easily because of the white mist that forms immediately in the presence of atmospheric moisture. Such leaks are usually promptly repaired.

Since sulfur dioxide has low solubility in common product acids (60° Bé and up) no appreciable amount escapes from product acid storage tanks. The acid condensed in the cold gas purification system of metallurgical type plants is relatively weak and cool, however, and under these conditions it contains substantial amounts of sulfur dioxide. In this type of plant, gas purification equipment is under vacuum and no appreciable leakage occurs.

When oleum is produced, acidic gases may be vented to the atmosphere from process and product oleum storage tanks. The emissions are most acute during loading of the tank truck or tank car. When air in the tank is displaced by oleum, sulfur trioxide vapor is vented to atmosphere in the form of white acid mist. The amount of sulfur trioxide emitted is reduced by a submerged transfer technique. In some plants, piping is installed for venting the displaced acidic gases into the acid plant. Another control method entails scrubbing the displaced vapor with 98 percent acid in a packed tower.

### Process Control Methods for Sulfur Compounds

Sulfur Dioxide — In a contact plant, essentially all of the unconverted sulfur dioxide leaving the converter passes through the absorption system to atmosphere. The quantity and concentration of sulfur dioxide emissions are dependent upon the catalyst converter and are related to the following factors:

1. Concentration of sulfur dioxide in the gases entering the converter and the ratio of oxygen to sulfur dioxide particularly in the last converter stage.
2. Number of catalyst converter stages.
3. Volume and distribution of catalyst in various converter stages.
4. Catalyst efficiency.
5. Uniformity of gas composition.
6. Impurities in the entering gas.
7. Temperature control at various points in the converter (This depends in part on having properly sized interstage gas-cooling equipment).

The minimum process control usually provided consists of temperature-indicating instruments and chemical means for determining the concentrations of sulfur dioxide in gases entering and leaving the converter. Usually the standard Reich test is used for sulfur dioxide analysis. Maximum instrumentation consists of temperature-indicating and recording instruments, air and sulfur flow indicators or recorders, and analyzers and recorders for the concentrations of sulfur dioxide entering the converter and leaving the 98 percent absorber. Analytical equipment for conducting the Reich test or equivalent is included to check the accuracy of the recorders. A few contact plants are equipped with a modified smoke-density recorder for the absorber exit gases.

In air dilution plants, apparatus is also provided for determining oxygen concentration of the gas leaving the converter or the absorber.

In addition to the above-listed instruments, most contact plants use interlocks that automatically shut the plant down in the event of an operating emergency. Safety interlocks may be provided for shutting down the combustion air blower and sulfur feed pumps in case of:

1. Failure of the 98 percent absorber feed pump.
2. Very low acid depth in absorber acid distributor.
3. Excessively low or high water level in the waste heat boiler.
4. Excessively high temperature in the equipment.

Sulfuric Acid Mist — The emission of acid mist is a minor part of the over-all acid plant yield. Because of the small size of the particles in an acid mist, however, the emissions are easily observed. Many factors cause formation of acid mist, and no single panacea can eliminate them. The chief factors responsible for formation and subsequent emission of acid mist are:

1. Improper concentration and temperature of the absorbing acid.
2. Amount and concentration of oleum produced.
3. High content of organic matter in the raw materials of a sulfur-burning plant.
4. High moisture content of sulfur dioxide gases entering the converter.
5. Shock cooling of sulfur trioxide gases leaving the converter, i.e., sudden chilling below the acid dew point, resulting in condensation of very small particles.
6. Presence of nitrogen oxides, which can result from excessive temperatures in the combustion chamber, from raw materials, and from arcing of electrical precipitators.
7. Insufficient rate of acid circulation and lack of uniformity in acid distribution.
8. Improper type or unclean packing in the 98 percent absorber.

Of all the readily controllable factors, the most important is probably the concentration and temperature of the 98 percent absorber acid. Since fluctuation may occur in the concentration and temperature of the absorber acid, it is watched most closely by the operator.

If acid-mist emissions from the absorber exit stack result in a heavy plume, changes in plant operation, raw materials, or design may be needed to reduce or eliminate stack plume opacity. Appendix C presents a tabulation of "Methods of Determining Causes of Visible Plumes From Stacks of Contact Acid Plants." In addition to these causes, the tabulation lists various measures for improving stack appearance.

Sulfuric Acid Spray — In most modern contact units, acid spray is not a problem. If an acid-spray emission occurs, it is normally the result of operating appreciably above design rate or of poor absorber design or excessive gas velocity in the absorber exit stack.

Use of Tall Stacks — One method for controlling emissions of sulfur dioxide and acid mist is the use of high stacks. The average acid plant stack is between 40 and 100 feet high; a few have been built as high as 400 feet.

The effective height of a stack can be increased by adding hot air or waste combustion gases. Hot air recovered from process equipment is used occasionally to dilute and heat the stack gas.

Large-size particles may be removed by increasing stack height or reducing stack gas velocities. Part of the entrained acid is removed either by impingement on the stack wall or by gravitational settling.

A series of test results shown in Table A4 for one sulfur-burning unit equipped with a 250-foot-high stack showed a decrease in concentration of acid mist and spray from 27 milligrams per cubic foot leaving the absorber to 2 milligrams per cubic foot at the top of the stack. Thus, 91 weight percent of total acid mist and spray from the absorber was recovered in the stack. Most of the reduction in acid-spray concentration was achieved by removal of large acid-mist particles. Essentially no reduction in acid particles of small size (true acid mist) was effected.

In order to determine the amounts of acid mist collected in the stacks of contact sulfuric acid plant absorbers, the total acid collected in the bases of stacks was measured daily at four different plants. The results of these measurements and process operating conditions are shown in Table A5. The steel absorber stacks for each plant were approximately 200 feet high. The tests were conducted during the winter when appreciable cooling of the stack and the acid mist was encountered. The weight percent of total acid mist and spray from the absorber that was collected in the stack as acid drip ranged from 0 to 11 percent.

The amount of acid collected for plant 1, 22 pounds per day, was over twice that collected by plant 2, 9 pounds per day. No acid drip was collected at plants 3 and 4. The difference between ambient and stack gas temperature was highest for plant 1, which collected 22 pounds per day of acid drip. However, the temperature differential was greater for plants 3 and 4, which collected no acid drip, than for plant 2, which collected 9 pounds per day.

Plants 1 and 3 were equipped with Teflon® mist eliminators, whereas plants 2 and 4 were not. Based on these limited observations, the amount of acid mist collected in the absorber stacks does not appear to be affected significantly by, (1) temperature difference between ambient air and stack gas or (2) the use of acid mist eliminators.

The velocity of the stack gases for these four plants varied from 775 to 1990 feet per minute. These velocities were appreciably lower than the 2820 foot-per-minute velocity for the 250-foot high stack. Thus, lower emissions of entrained acid mist and spray would be expected. Apparently the entrainment of large acid-mist particles from the absorber is the main source of acid drip in the absorber stack.

### Ancillary Techniques for Recovery and Emission Control

Sulfur Dioxide — Plants are usually designed to minimize acidic gas emissions to the atmosphere. Since addition of auxiliary equipment increases capital expenditures and operating costs, many plants today operate with little or no recovery equipment.

Many types of recovery processes have been proposed, but only rarely are they installed. The Cominco® (ammonia scrubbing) process is used in only two plants in the United States. The process reduces $SO_2$ concentration in exit gases to about 0.08 percent for single-stage units or to about 0.03 percent for two-stage units.

Although this process is highly efficient for removal of $SO_2$, it is inefficient in removal of acid mist. The ammonia scrubbing equipment must be supplemented with mist-removal equipment if mist is also a problem.

During World Wars I and II, the $SO_2$ content of exit gases of contact plants was used to some extent to make sodium sulfite-bisulfite solution to wash trinitrotoluene. In this process the gases were scrubbed with sodium carbonate solution; the process appears to have no utility in peacetime.

Scrubbing with fresh or salt water removes half to two-thirds of the $SO_2$ but may present problems in the use or disposal of the resulting solution.

Sulfuric Acid Mist and Spray — A number of devices of varying cost and efficiency are in use for removal of acid mist and spray from absorber tail gases. With any of them, relatively high efficiencies (over 90 percent) do not necessarily result in an invisible plume unless there are few particles less than 3 microns and unless inlet mist loading is not excessive. The following comments apply to devices used successfully on a commercial scale.

(1) *Wire-Mesh Mist Eliminators*

The lowest-first-cost device that effectively removes particles larger than about 3 microns diameter is the wire-mesh eliminator. Particle size and possibilities of corrosion from concentrated sulfuric acid mist must be carefully considered when selecting a wire-mesh eliminator. The eliminator is commonly constructed with two beds in series and operates with pressure drops of 1 to 3 inches of water. Test results for a two-stage wire-mesh eliminator, given in Table A3, show an acid-mist collection efficiency of 92.6 percent. The collection efficiency decreased to 37.3 percent, however, when oleum was produced. In this case, 62 percent of the particles were smaller than 3 microns. Although no plume was visible during production of 98 percent acid, a plume was plainly visible when oleum was also being produced.

Massey (*13*) reports the following results (Table 5) for a system using a two-stage alloy wire-mesh unit operating at a gas velocity of 12 to 15 feet per second. No oleum was produced.

TABLE 5. EFFECT OF WIRE-MESH MIST ELIMINATORS ON ACID-MIST COLLECTION

| Pressure drop, inches water | Acid mist, milligrams per cubic foot of tail gas | | Acid mist collection efficiency, % |
|---|---|---|---|
| | Inlet | Outlet | |
| ¾ | 4.1 | 0.74 | 82.0 |
| 1 | 8.8 | 0.7 | 92.5 |
| 1¼ | 13.8 | 0.92 | 93.4 |
| 1¼ | 66.9 | 0.77 | 98.9 |
| 1½ | 32.5 | 0.98 | 97.0 |
| 1½ | 13.0 | 0.76 | 94.1 |
| AVERAGE | 23.2 | 0.81 | 96.5 |

### (2) *Fiber Mist Eliminators*

The high-effciency glass-fiber mist eliminator is capable of operating with acid-mist collection efficiencies of over 99 percent. The data for plants 5, 6, and 7 (Table A3) show acid-mist collection efficiencies for glass-fiber eliminators ranging from about 50 to 99.9 percent. The lower collection efficiencies for plant 5 were obtained with a glass-fiber unit specifically designed for collection at high velocity and medium efficiency. A high-efficiency glass-fiber unit was utilized in plant 7. For this plant, an acid-mist collection efficiency of 99.9 percent was obtained for a tail gas stream in which 38 percent of the particles, by weight, were 3 microns and smaller. The pressure drop for a high-efficiency glass-fiber mist eliminator is usually between 5 and 10 inches of water, but the system may be designed for higher or lower pressure drops, depending upon relative costs for power and equipment.

The glass-fiber mist eliminator is also capable of maintaining a high mist-collection efficiency at varying tail gas flow rates. Maintenance expense is low.

Table 6, from Brink(*12*), gives data for collection of sulfuric acid mist in a sulfur-burning contact plant with a glass-fiber mist eliminator.

### (3) *Electrostatic Precipitators*

Electrostatic precipitators are highly efficient when used for collection of acid mist regardless of size of the acid-mist particles. The acid-mist collection efficiencies for precipitators in plants 3 and 4 (Table A3) ranged from 92.2 to 99.9 percent.

Precipitators operate with pressure drops less than 1 inch of water and may be either of the wet or dry type. The dry type, which is suitable only for concentrated acid, is much less expensive but more susceptible to corrosion. Wet-type precipitators are suitable for use only with dilute acid and thus necessitate prior humidification of stack gases. Pre-humidification also permits removal of sulfur trioxide by converting it to acid mist. The humidification step appreciably increases the cost of a wet-type installation.

### (4) *Ceramic Filters*

The ceramic filter, a German device, is reported to operate with highly efficient acid-mist collection at constant tail gas flow rates. Pressure drop is of the order of 10 to 12 inches of water. The filter has not been accepted in commercial installations in the United States because of high maintenance costs and inflexibility in handling varying gas volumes.

### (5) *Venturi Scrubbers*

Venturi scrubbers are also capable of operating with high acid-mist collection efficiency, but at the expense of high pressure drop. The scrubbers are also able to remove unabsorbed sulfur trioxide. Exit acid-mist loadings ranging from 0.5 to 3 milligrams per cubic foot have been reported by one manufacturer at pressure drops of 28 to 35 inches of water when used on sulfuric acid concentrators(*14*). Venturi scrubbers have not been used on exit gases from contact acid plants.

### (6) *Packed-Bed Separators*

In the past contact plants commonly included a packed-bed "spray catcher" above the acid distributor in the absorber primarily to remove entrained particles of spray by impingement. The spray catcher is not efficient in removing acid mist. Although some plants have used an external packed bed for exit gas streams, none are known to be operating in this service today.

TABLE 6. COLLECTION OF $H_2SO_4$ MIST FROM A SULFUR-BURNING CONTACT SULFURIC ACID PLANT WITH FIBER MIST ELIMINATORS(*12*)

| Contact plant production | Mist loading[a] of gases leaving absorber and entering mist, eliminator, mg $H_2SO_4$/scf | Mist loading[a] of gases leaving mist eliminator, mg $H_2SO_4$/scf | Particle collection efficiency ($3\mu$ and smaller), % |
|---|---|---|---|
| | | Mist Eliminator A[b] | |
| 99% $H_2SO_4$ and 65% oleum at full capacity | 30.9 | 1.50 | 95.1 |
| | 31.8 | 1.48 | 95.3 |
| | 39.9 | 1.64 | 95.9 |
| 99% $H_2SO_4$ and 25% oleum at 75% capacity | 6.55 | 0.124 | 98.1 |
| | 8.75 | 0.169 | 98.1 |
| | 6.64 | 0.125 | 98.1 |
| | | Mist Eliminator B[b] | |
| 99% $H_2SO_4$ and 25% oleum at full capacity | 14.4 | 0.085 | 99.4 |
| | 18.3 | 0.112 | 99.4 |
| | 19.3 | 0.095 | 99.5 |
| 99% $H_2SO_4$ and 25% oleum at 60% capacity | 6.88 | 0.045 | 99.3 |
| 99% $H_2SO_4$ at 60% capacity | 2.12 | 0.014 | 99.3 |

[a] The mist-loading values are limited to particles 3 microns in diameter and smaller.

[b] Mist eliminator A was designed for 100 percent efficiency for particles larger than 3 microns diameter and for 95 percent efficiency for particles 3 microns and smaller, operated at a pressure drop of 3 inches of water. Mist eliminator B was designed for 100 percent efficiency for particles larger than 3 microns and for 99 percent efficiency on particles 3 microns diameter and smaller, operated at a pressure drop of 6 inches of water.

# SUMMARY OF SAMPLING AND ANALYTICAL TECHNIQUES

A variety of stack-sampling and analytical procedures have been used by various sulfuric acid manufacturers, by air pollution control districts, and by the joint Manufacturing Chemists' Association — Public Health Service field-test team in obtaining the emission data shown in Tables A1 and A3. Detailed descriptions of these sampling and analytical procedures are presented in Appendix B.

## SULFURIC ACID MIST

Many of the contact acid plants use the Monsanto Company Method for collection and analysis of sulfuric acid mist*(15)*.

This technique, with several modifications, was also used by the joint MCA-PHS field test team. Effluent gas samples were collected in the duct or exit stack just above the acid absorber. Pitot tube traverses were made to determine the velocity profile of the gases in the duct. Sampling was performed isokinetically at a number of traverse points. The stack gases were drawn through a glass sampling train consisting of a probe, a cyclone collector, and a glass-fiber mist collector. Both the probe and enclosed sample train were heated to preclude condensation in the sample gas stream. The cyclone collected acid-mist particles larger than 3 microns. The particles smaller than 3 microns were collected on the fine glass-fiber filter. Analysis for sulfuric acid mist in both the cyclone and the glass-fiber filter tube was performed by titrating with dilute caustic to a phenolphthalein end point.

A few of the plants for which data are reported employed medium-porosity fritted glass disks, or millipore or Whatman filters for collection of sulfuric acid mist. In each case analysis was performed by titrating with dilute caustic to a phenolphthalein end point.

## SULFUR DIOXIDE AND SULFUR TRIOXIDE

The most commonly used method for sulfur dioxide analysis in sulfuric acid plants is the Reich test*(16)*. This test is normally performed by the acid plant operator at least once during his work shift. Most of the acid plants for which data are reported utilized the Reich test for determining the sulfur dioxide concentration in the stack gas. Analysis was conducted by passing a measured volume of stack gas through a known quantity of iodine solution containing starch until the blue color disappeared. In some cases the sulfur dioxide concentrations were determined from gas samples collected an hour before or after the acid-mist samples under essentially the same operating conditions.

The Shell Development Method was used by the joint MCA-PHS field test team for sample collection and analysis of both sulfur dioxide and sulfur trioxide*(17)*. Sample gas was first drawn through a glass-wool filter, then passed through a heated glass probe into a system of three sintered glass plate absorbers. The first absorber was immersed in an ice bath. The first two absorbers contained an isopropyl alcohol - water solution for absorption of sulfur trioxide. The third absorber contained dilute hydrogen peroxide in water for absorption of sulfur dioxide. Purified air was passed through the absorbers at the end of the run to remove any dissolved sulfur dioxide in the first two absorbers. Any sulfur dioxide removed was absorbed by hydrogen peroxide in the third absorber. Analysis was conducted by titrating each solution with standard barium chloride using thorin indicator.

The Chemical Construction technique was used to determine the sulfur dioxide and sulfur trioxide concentrations shown for plants 3 and 16 (Table A2) (*18*). Sample gas was drawn through a glass probe and tray into a system consisting of two glass-fiber filters held by a fritted glass disk. Two bubblers with coarse-fritted glass gas distributors and a flow meter completed the sampling train. Each bubbler contained a standardized solution of hydrogen peroxide in water. At the conclusion of sampling, the absorbing solution in the two impingers was transferred to a volumetric flask and diluted to the mark. Half of this solution was titrated with standard potassium permanganate for unused hydrogen peroxide. The difference in titration between the standard hydrogen peroxide solution and the sample yielded the sulfur dioxide concentration. The other half of the sample solution was titrated with standard caustic for total concentration of sulfur dioxide and sulfur trioxide. The sulfur trioxide concentration was determined by difference.

The sulfur dioxide concentration for plants 5A and 5B (Table A3) was determined by the Reich method. The sulfur trioxide in this sample gas stream was absorbed in an isopropyl alcohol - water solution contained in Greenberg-Smith impingers. Analysis was made by titration with standard barium chloride.

The sulfur dioxide concentration for plant 19 (Table A2) was determined by the Reich method. The sample gas was drawn through a fine-fritted glass disk for collection of acid mist. The acid-mist concentration was determined by titration with dilute caustic. A second acid-mist sample was collected by the same procedure after the sample gas stream had been humidified to hydrate the sulfur trioxide. Analysis for total acid mist and sulfur trioxide was then made by titration with dilute caustic. The sulfur trioxide concentration was determined by difference.

## OXIDES OF NITROGEN

Total nitrogen oxide concentration was determined in all tests by the Bureau of Mines phenoldisulfonic acid method (*19*), which is free from interference by sulfur dioxide. The sample was drawn through a glass probe and collected in an evacuated 2-liter flask containing a dilute solution of sulfuric acid and hydrogen peroxide. After sampling, the resultant solution was neutralized, evaporated to dryness, and treated with phenoldisulfonic reagent and ammonium hydroxide. The yellow trialkali salt formed was measured colorimetrically.

Nitrogen dioxide was determined by the Saltzman technique (*20*). The gas sample was collected in a syringe containing Saltzman reagent. After the syringe was shaken for 1 minute the gas was expelled, and after 15 minutes the concentration of nitrogen dioxide was measured colorimetrically. This technique minimizes the interference caused by air oxidation of nitrogen oxide to nitrogen dioxide and by sulfuric dioxide.

After the concentrations of total nitrogen oxides and of nitrogen dioxide were determined by the phenoldisulfonic acid and the Saltzman techniques, respectively, the concentration of nitric oxide was determined by difference.

# GLOSSARY OF TERMS

| | |
|---|---|
| °Bé | degrees Baumé (Specific gravity $= \frac{145}{145 - °Bé}$) |
| °C | temperature, degrees Centigrade |
| cf, $ft^3$, cu ft | cubic feet |
| cfm | cubic feet per minute, measured at actual temperature and pressure |
| °F | temperature, degrees Fahrenheit |
| ft/min | feet per minute |
| gr | grain (1 grain equals 64.8 milligrams) |
| in. $H_2O$ | inches of water |
| in. Hg | inches of mercury |
| lfm | linear feet per minute measured at actual temperature and pressure |
| mg | milligram |
| ml | milliliter |
| mm | millimeter |
| Mscfm | 1000 standard cubic feet per minute |
| psig | pounds per square inch gage |
| °R | temperature, degrees Rankine (°F plus 460 degrees) |
| ® | registered trade mark |
| scf | standard cubic feet measured at 0°C (32°F) and 760 mm (29.92 in.) Hg |
| scfm | standard cfm, measured at 0°C (32°F) and 760 mm (29.92 in.) Hg |
| slfm | standard linear feet per minute, measured at 0°C (32°F) and 760 mm (29.92 in.) Hg |
| sp. gr. | specific gravity |

*CHEMICAL SYMBOLS*

| | |
|---|---|
| $H_2$ | hydrogen |
| $H_2O$ | water |
| $H_2S$ | hydrogen sulfide |
| $H_2SO_4$ | sulfuric acid (monohydrate of sulfur trioxide or 100 percent acid) |
| Hg | mercury |
| $N_2$ | nitrogen |
| $NH_3$ | ammonia |
| NO | nitric oxide |
| $NO_2$ | nitrogen dioxide |
| $O_2$ | oxygen |
| S | sulfur |
| $SO_2$ | sulfur dioxide |
| $SO_3$ | sulfur trioxide |
| $SO_5NH$ | nitrosylsulfuric acid "nitrose" |

## DEFINITIONS

| | |
|---|---|
| *Absorber* | The absorber in the contact process is a corrosion-resistant brick-lined steel tower usually packed with partition rings. |
| *Baumé* (Bé) | Acid strength is determined by use of a floating instrument (hydrometer) calibrated to read degrees Baumé and by a conversion chart. The Baumé can also be calculated if the specific gravity of the sulfuric acid is known:<br>$°\text{Bé} = 145 - \left(\frac{145}{\text{sp. gr.}}\right)$ |
| *Catalyst* | The catalyst in a chamber plant is gaseous nitrogen oxides. In the contact process the catalyst is a solid, consisting of vanadium pentoxide and various promotors deposited on a highly porous siliceous carrier. |
| *Chamber acid* | Sulfuric acid made by the chamber process with strength not exceeding 60° Baumé (77.67 percent). |
| *Converter* | The vessel that houses the solid vanadium catalyst. The catalyst is placed in several horizontal trays or stages located in series, with means for gas cooling between the various stages. |
| *Crude sulfur* | A low-sulfur-content raw material consisting of a mixture of elemental sulfur and inert material. |
| *Elemental sulfur* | Any sulfur in elemental form, regardless of source. |
| *Frasch-process sulfur* | A high-purity sulfur containing not more than 0.01 percent ash and from 0.05 percent or less to 1.0 percent hydrocarbons, with no free water or acid when mined. (If shipped molten, it may also contain traces of hydrogen sulfide.) |
| *New or virgin acid* | Sulfuric acid made from elemental sulfur or other sulfur-bearing materials, but not from spent acid strengthened by addition of sulfur trioxide. |
| *Niter or nitre* | A term used loosely concerning chamber plants and having many meanings. It can refer to equivalent consumption of 96 percent pure nitrate of soda ($NaNO_3$), nitric acid ($HNO_3$), and ammonia ($NH_3$), or any of the oxides of nitrogen. |
| *Nitrose or nitrous vitriol* | Sulfuric acid from the Gay Lussac tower, containing 1 to 2 percent oxides of nitrogen. |
| *Oleum or fuming sulfuric acid* | A solution of free, uncombined sulfur trioxide ($SO_3$) in sulfuric acid ($H_2SO_4$), e.g. 20 percent oleum refers to a solution containing 20 percent free sulfur trioxide and 80 percent sulfuric acid. Oleum is sometimes referred to as over 100 percent |

acid; thus, 20 percent oleum may be called 104.5 percent sulfuric acid. This means that if enough water were added to 100 parts of 20 percent oleum to combine with the free sulfur trioxide, 104.5 parts of sulfuric acid would be obtained.

| | |
|---|---|
| *Particle size* | Refers to equivalent diameter assuming that the particles are spheres. |
| *Plant, unit, establishment* | The word plant, as used herein, is synonymous with unit. The word establishment herein denotes a works in which there may be one or more sulfuric acid plants or units, each being a complete production entity. |
| *Recovered sulfur* | An extremely high-purity sulfur containing no organic matter, less than 0.005 percent ash, and no free acid or water unless exposed to the atmosphere. (If shipped molten, it may also contain traces of hydrogen sulfide.) |
| *Regenerated acid* | High-purity sulfuric acid made from decomposition or regeneration of spent acid from petroleum refineries or other chemical processes. |
| $SO_2$ *gas or* $SO_3$ *gas* | A gas in which $SO_2$ or $SO_3$ is present with other constituents such as oxygen or nitrogen. |
| *Sulfur oxides* | As used in this report, sulfur oxides include sulfur dioxide and sulfur trioxide, and/or sulfuric acid mist or spray. |
| *Sulfuric acid mist* | Extremely small acid particles that are true aerosols. No exact range of particle size is available. The "Modified Monsanto Company Technique" (Appendix B) arbitrarily distinguishes between the percentage of particles greater than 3 microns diameter and of those 3 microns and smaller. |
| *Sulfuric acid spray* | Large acid particles introduced into the gas by mechanical entrainment. If emitted to atmosphere, they are invisible and fall rapidly to the ground. See "Stick Test," Appendix B. |
| *Yield* | The molar percent conversion of sulfur and/or sulfur dioxide into sulfuric acid. |

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# APPENDIX A: EMISSION AND OPERATING DATA FOR CHAMBER AND CONTACT SULFURIC ACID PLANTS

Most of the emission and operating data in Appendix A were supplied by the major manufacturers of sulfuric acid. Data from essentially all types of sulfuric acid plants are included. The emission data represent results from approximately 12 percent of the present number of establishments and include results from stack-sampling programs conducted jointly by the Manufacturing Chemists' Association and the Public Health Service.

## TABLE A1. EMISSION AND OPERATING DATA FOR CHAMBER SULFURIC ACID PLANTS[a]

| Raw material | Molten dark sulfur | Solid sulfur |
|---|---|---|
| Plant number | 1 | 2 |
| $H_2SO_4$ production, tons/day | 113 | 29 |
| Percent of maximum plant capacity | 90 | 80 |
| Stack gas temperature, °F | 105 | 105 |
| Stack gas rate, Mscfm[b] | 12.5 | 1.9 |
| $O_2$ in stack gas, vol % | 16.5 | 8.3 |
| $SO_2$ in stack gas, vol % | 0.087 | 0.164 |
| $SO_2$ emitted, tons/day | 1.40 | 0.41 |
| $NO_2$ in stack gas, vol % | 0.123 | 0.048 |
| Total $NO_x$ in stack gas, vol %[c] | 0.185 | 0.099 |
| Total $NO_x$ emitted, tons/day | 2.12 | 1.14 |
| $H_2SO_4$ mist leaving Gay-Lussac tower, mg/scf | 5.3 | 28.2 |
| Total acid mist leaving Gay-Lussac tower, mg/scf[d] | 5.9 | 33.0 |
| Total acid mist leaving Gay-Lussac tower, tons/day | 0.12 | 0.10 |
| Acid mist, % less than 3 micron diameter | 10.1 | 3.5 |
| Stack plume opacity | Medium | Medium |

[a] Sampling points were in duct or exit stack near top of Gay Lussac Tower. Data for each plant are averages of four tests conducted by joint MCA-PHS field test team.

[b] All volumes corrected to 32°F and 29.9 in. Hg.

[c] Total $NO_x$ measured at $NO_2$.

[d] Total acid mist measured as $H_2SO_4$ and $HNO_3$.

## TABLE A2. EMISSION AND OPERATING DATA FOR CONTACT SULFURIC ACID PLANTS WITHOUT MIST ELIMINATORS[a]

| Plant type | Sulfur burning, air dilution | | | | | | | | Sulfur burning, no air dilution | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| Raw material | Molten dark | | | | | Molten recovered | | | Molten recovered | | | |
| Plant number | 1 | 2A[d] | 2B | 3 | 4 | 5 | 6A | 6B | 7A | 7B | 7C | 8[e] |
| $H_2SO_4$ production, tons/day | 735 | 650 | 650 | 120 | 422 | 130 | 100 | 100 | 325 | 325 | 162 | 115 |
| Percent of maximum plant capacity | 98 | 100 | 100 | 80 | | 100 | 77 | 77 | 100 | 100 | 50 | 30 |
| Oleum made, % of output | 0 | 0 | 25 | 50 | 51 | 0 | 0 | 0 | 43 | 43 | 35 | 0 |
| Oleum made, % of free $SO_3$ | | | 20 | 20 | 30.8 | | | | 20 | 26 | 20-25 | 0 |
| Stack gas temperature, °F[f] | 212 | 175 | 175 | 115 | 123 | 175 | 173 | 168 | 148 | 148 | 140 | 94 |
| Stack gas rate, Mscfm | 45 | 48 | 48 | 7.6 | 25.1 | 7.5 | 6.5 | 6.5 | 16.7 | 16.6 | 11.0 | 5.9 |
| $SO_2$ entering converter, vol %[g] | 8.0 | 7.0 | 7.0 | 8.0 | 8.8 | 8.8 | 8.0 | 8.0 | 10.5 | 10.6 | 7.7 | 8.6 |
| $SO_2$ in stack gas, vol %[h] | 0.20 | 0.31 | 0.31 | 0.23 | 0.25 | 0.28 | 0.20 | 0.20 | 0.53 | 0.54 | 0.13 | 0.19 |
| Conversion of $SO_2$ to $SO_3$, % | 97.8 | 96.0 | 96.0 | 97.5 | 97.5 | 97.2 | 97.8 | 97.8 | 95.7 | 95.6 | 98.5 | 98.1 |
| $SO_2$ emitted, tons/day | 11.5 | 19.0 | 19.0 | 2.2 | 8.0 | 2.7 | 1.7 | 1.7 | 11.3 | 11.5 | 1.8 | 1.4 |
| Acid mist leaving absorber, mg/scf | 2.37 | 15.5 | 23.7 | 1.1 | 2.0-4.0 | 9.2 | 3.7 | 2.2 | 2.3 | 5.1 | 2.5 | 2.3 |
| Acid mist, % less than 3 microns | 25 | 9.5 | 54 | | | 80 | 81 | 82 | 80 | 87 | | |
| Acid mist emission from absorber, tons/day | 0.17 | 1.13 | 1.81 | | 0.12 | 0.11 | 0.04 | 0.02 | 0.06 | 0.13 | 0.04 | 0.02 |
| $SO_3$ concentration leaving absorber mg/scf | | | | 19.2 | | | | | | | [i] | |
| Plume opacity | none | med | dns | | lt | fnt | none | none | lt | med | | med |

[a] Sampling points:

Plant 11: In horizontal duct leading to remote stack about 100 feet from absorber.

Plant 19: In stack about 35 feet above absorber.

All other plants: In duct or exit stack near top of absorber. (All plants incorporate internal, packed bed "spray" eliminators as part of the standard absorber design.)

[b] Pyrite or pyrrhotite.

[c] Byproduct $SO_2$ gas from decomposition of sulfates.

[d] Plant numbers followed by letters indicate tests made in the same plant under different operating conditions. Thus, plants 2A and 2B represent the same plant.

TABLE A2 (Continued)

| Plant type | Sulfur burning, no air dilution | | | | Metallurgical | | | Spent acid | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|
| Raw material | Solid | | Molten dark | | Pyr't spent acid | Pyr't[b] | By-prod. gas[c] | Spent acid and sulfur | | Spt. acid | Spent acid, $H_2S$, sulfur |
| | Brt. | Dk. | | | | | | | | | |
| Plant number | 9 | 10 | 11 | 12 | 13 | 14 | 15 | 16 | 17 | 18 | 19 |
| $H_2SO_4$ production, tons/day | 210 | 500 | 310 | 265 | 285 | 500 | 100 | 650 | 302 | 900 | |
| Percent of maximum plant capacity | 100 | 100 | 100 | 88 | 100 | 100 | 70 | 91 | | 100 | 91 |
| Oleum made, % of output | 0 | 40 | 100 | 33 | 25 | 0 | yes | 77 | 71.5 | 0 | 18 |
| Oleum made, % of free $SO_3$ | | 25 | 25 | 38 | 26 | | | 20 | 20 | 0 | 20 |
| Stack gas temperature, °F[f] | | 170 | 105 | 170 | 190 | | | 136 | 163 | 145 | 178 |
| Stack gas rate, Mscfm | 12.0 | 30.0 | 17.0 | 14.0 | 18.2 | 35 | 5.0 | 58.5 | 19.7 | 62 | 34 |
| $SO_2$ entering converter, vol %[g] | 9.1 | 10.2 | 9.0 | 10.0 | 8.0 | | | 8.8 | 8.0 | 7.5 | 6.7 |
| $SO_2$ in stack gas, vol %[h] | 0.24 | 0.40 | 0.25 | 0.42 | 0.23 | | | 0.37 | 0.20 | 0.34 | 0.20 |
| Conversion of $SO_2$ to $SO_3$, % | 97.7 | 96.7 | 97.6 | 96.5 | 97.5 | | | 96.3 | 97.8 | 95.9 | 97.3 |
| $SO_2$ emitted, tons/day | 3.7 | 15.4 | 5.4 | 7.5 | 5.4 | | | 27.7 | 5.0 | 27.0 | 8.7 |
| Acid mist leaving absorber, mg/scf | 9.5 | 6.1 | 1.9 | 37.3 | 6.0 | 33.2 | 13.7 | 8.4 | 10-12 | 10.2 | 7.0 |
| Acid mist, % less than 3 microns | | 78 | 91 | 95 | | 14 | 91 | | | 90 | |
| Acid mist emission from absorber, tons/day | 0.18 | 0.29 | 0.05 | 0.83 | 0.17 | 1.84 | 0.11 | 0.78 | 0.34 | 1.00 | 0.38 |
| $SO_3$ concentration leaving absorber mg/scf | | | | | [i] | | | 48.0 | | | 0.5 |
| Plume opacity | lt | med | med | dns | | dns | med | | | dns | |

[e] This plant uses an impingement type of separator in the stack, which removes mainly spray.

[f] Some of the temperatures are of acid entering the absorbers; however, outlet gas and inlet acid temperatures are usually close together.

[g] In the air dilution type of plant, this is the equivalent percent $SO_2$ after correction for air dilution.

[h] Some of the concentrations of $SO_2$ were obtained from samples collected either before or after the acid mist samples but under essentially the same operating conditions.

[i] Unabsorbed $SO_3$ is included as part of the concentration of acid mist leaving the absorber.

## TABLE A3. EMISSION AND OPERATING DATA FOR CONTACT SULFURIC ACID PLANTS WITH MIST ELIMINATORS[a]

| Plant type | Sulfur | | | Combination | | | |
|---|---|---|---|---|---|---|---|
| | Air dil. | No air dil. | | | | | |
| Raw material | Molten dark | | | Spent acid, $H_2S$, and supplemental sulfur | | | |
| Plant number | 1 | 2A[b] | 2B[b] | 3A | 3B | 3C | 4 |
| $H_2SO_4$ production, tons/day | 961 | 150 | 150 | 240 | 240 | 219 | 133 |
| Percent of maximum capacity | 96 | 68 | 68 | 100 | 100 | 91 | 60 |
| Oleum made, % of output | 0 | 0 | 13 | 0 | 0 | 0 | 56 |
| Oleum made, % of free $SO_3$ | 0 | 0 | 30 | | | | 40 |
| Stack gas temperature, °F[d] | 186 | 165 | 166 | 180 | 180 | 76 | 76 |
| Stack gas rate, Mscfm | 58 | 7.4 | 7.4 | | | 12 | 7 |
| $SO_2$ entering converter, vol % | 8.0 | 8.0 | 8.0 | | | 8.2 | 8.4 |
| $SO_2$ in stack gas, vol % | 0.14 | 0.19 | 0.20 | 0.34 | 0.35 | 0.26 | 0.17 |
| Conversion of $SO_2$ to $SO_3$, % | 98.5 | 97.6 | 97.5 | | | 97.2 | 98.2 |
| $SO_2$ emitted, tons/day | 10.4 | 1.8 | 1.9 | | | 4.0 | 1.5 |
| Type of mist eliminator | Wire mesh | | | Electrical precipitator | | | |
| Acid mist leaving absorber, % less than 3 microns | 70 | 7.5 | 62.0 | | | | |
| Acid mist leaving absorber, mg/scf | | 48.8 | 37.3 | 5.9 | 4.9 | 7.1 | 29.0 |
| Acid mist leaving mist eliminator, mg/scf | 6.5 | 3.6 | 23.4 | 0.33 | 0.38 | 0.18 | 0.31 |
| $H_2SO_4$ collection efficiency, % | | 92.6 | 37.2 | 94.5 | 92.2 | 97.5 | 99.9 |
| $H_2SO_4$ emitted, tons/day | 0.60 | 0.04 | 0.27 | | | 0.003 | 0.003 |
| $SO_3$ concentration leaving absorber mg/scf | | 2.1 | 1.0 | | | | |
| $SO_3$ concentration leaving mist eliminator, mg/scf | | 1.1 | | | | | |
| Plume opacity | light | none | med. | light | light | light | light |

[a] Sampling points:
Plant 6A and 6B: in horizontal duct between absorber top and exit stack.
All other plants: in duct or exit stack near top of absorber.

[b] Test data for Plant 2A and 2B were obtained by joint MCA-PHS field testing. The results are averages of several tests.

TABLE A3 (Continued)

| Plant type | Combination | | | | Wet gas | Sulfur | Combination |
|---|---|---|---|---|---|---|---|
| Raw material | Spent acid, $H_2S$, and supplemental sulfur | | | | $H_2S$ sulfur | Molten dark | Spent acid, sulfur |
| Plant number | 5A | 5B | $6A^c$ | $6B^c$ | 7 | 8 | 9 |
| $H_2SO_4$ production, tons/day | 300 | 300 | 265 | 300 | 100 | 429 | 272 |
| Percent of maximum capacity | 76 | 76 | 88 | 100 | 67 | | |
| Oleum made, % of output | 0 | 2 | 0 | 0 | 0 | 13 | 0 |
| Oleum made, % of free $SO_3$ | | 25 | | | | 21.5 | |
| Stack gas temperature, °F[d] | 175 | | 160 | 180 | 130 | 176 | 150 |
| Stack gas rate, Mscfm | 17 | | 14 | 21 | 11 | 28.0 | 19.3 |
| $SO_2$ entering converter, vol % | 9.0 | | 7.2 | 7.4 | | 8.0 | 7.4 |
| $SO_2$ in stack gas, vol % | 0.32 | | 0.16 | 0.19 | | 0.19 | 0.20 |
| Conversion of $SO_2$ to $SO_3$, % | 96.9 | | 98.0 | 97.8 | | 98.0 | 96.7 |
| $SO_2$ emitted, tons/day | 7.0 | | 2.8 | 5.1 | | 6.8 | 5.0 |
| Type of mist eliminator | | Glass fiber | | | | Teflon® mesh | |
| Acid mist leaving absorber, % less than 3 microns | | | | | 38 | | |
| Acid mist leaving absorber, mg/scf | 1-4[e] | 10-30[e] | 20.6 | 32 | 2533[f] | | |
| Acid mist leaving mist eliminator, mg/scf | 0.5-2 | 7-9 | 0.23 | 1.9 | 2.3 | 1-2 | 1-4 |
| $H_2SO_4$ collection efficiency, % | 50.0 | 60.0 | 98.9 | 94.1 | 99.9 | | |
| $H_2SO_4$ emitted, tons/day | 0.01-.05 | | 0.005 | 0.06 | 0.04 | | |
| $SO_3$ concentration leaving absorber mg/scf | 1-2 | | | | | | |
| $SO_3$ concentration leaving mist eliminator, mg/scf | 1-2 | | | | | | |
| Plume opacity | | | none | faint | light | faint | faint |

[c] Raw material included 48.4% spent acid, 32.8% $H_2S$, and 18.8% sulfur.

[d] Some of the temperatures are of acid entering the tower; however, inlet gas and acid temperatures are usually close together.

[e] High-velocity type glass-fiber mist eliminator designed for only medium performance.

[f] This "wet gas" unit utilized no water-removal facilities for the discharge combustion chamber gases.

### TABLE A4. CONCENTRATIONS OF SULFURIC ACID MIST AND SPRAY AT VARIOUS STACK ELEVATIONS

(Sulfur-Burning Plant with Molten Sulfur as Raw Material)

| | |
|---|---|
| Oleum, % of output | 0 |
| Stack height, ft | 250 |
| Stack gas velocity, ft/min | 2,820 |
| Stack gas temperature, °F | 180 |
| Stack gas rate, scfm[a] | 27,290 |
| $SO_2$ entering converter, vol % | 9.0 |
| Conversion of $SO_2$ to $SO_3$, % | 95.7 |
| $SO_2$ in stack gas, vol % | 0.39 |
| Concentration of acid spray at absorber outlet, mg/scf[b] | 26.65 |
| Concentration of acid mist at absorber outlet, mg/scf | 0.64 |
| Concentration of acid spray at 100-ft elevation in stack, mg/scf | 10.12 |
| Concentration of acid mist at 100-ft elevation in stack, mg/scf | 0.77 |
| Concentration of acid spray at 250-ft elevation in stack, mg/scf | 2.15 |
| Concentration of acid mist at 250-ft elevation in stack, mg/scf | 0.38 |
| Total acid mist and spray from absorber collected in stack, wt % | 91 |

[a] Volume corrected to 32°F and 29.9 in. Hg.

[b] All acid spray or mist concentrations are average values for three test runs. Acid spray included only that caught on inside of glass probe. Acid mist was collected in an asbestos filter.

### TABLE A5. ACID-MIST COLLECTION IN ABSORBER STACKS OF CONTACT SULFURIC ACID PLANTS[a]

| Raw material | Molten sulfur | | Molten sulfur and spent acid | |
|---|---|---|---|---|
| Plant number | 1 | 2 | 3 | 4 |
| $H_2SO_4$ production, tons/day | 429 | 422 | 272 | 302 |
| Oleum, % of output | 13 | 51 | 0 | 71.5 |
| Oleum, % of free $SO_3$ | 21.5 | 30.8 | 0 | 20.0 |
| Stack gas temperature, °F | 176 | 123 | 150 | 163 |
| Stack gas rate, Mscfm | 28.0 | 25.1 | 19.3 | 19.7 |
| $SO_2$ entering converter, vol % | 8.0 | 8.8 | 7.4 | 8.0 |
| Conversion of $SO_2$ to $SO_3$, % | 98.0 | 97.5 | 97.6 | 97.8 |
| $SO_2$ in stack gas, vol % | 0.19 | 0.25 | 0.20 | 0.20 |
| Ambient temperature (avg), °F | 25 | 29 | 42 | 35 |
| Ambient temperature (range), °F | 8-37 | 25-36 | | |
| Wind direction | NW, W, SW | N, NW, W | S-SE | S-SW |
| Wind velocity (avg), mph | 10.1 | 6.4 | 12 | 3 |
| Stack plume opacity | faint | light | faint | medium |
| Stack gas velocity, ft/min | 1990 | 1620 | 1080 | 775 |
| $H_2SO_4$ concentration leaving absorber, mg/ft$^3$[b] | | 2-4 | | 10-12 |
| $H_2SO_4$ concentration leaving Teflon demister, mg/ft$^3$[b] | 1-2 | no demister | 1-4 | no demister |
| Acid drip from base of stack, lb/day | 22 | 9 | 0 | 0 |
| Strength of acid drip, % $H_2SO_4$ | 70.4 | 99.5 | | |
| Total acid mist from absorber collected in stack, wt %[c] | 11.0 | 3.6 | 0 | 0 |

[a] All plants incorporate internal, packed bed "spray" eliminators as part of the standard absorber design.

[b] Acid mist concentrations are normal loadings, but were not obtained during acid drip measurements.

[c] The amounts of acid mist collected were averages from several tests conducted at each plant.

# APPENDIX B: SAMPLING AND ANALYTICAL TECHNIQUES

The sampling and analytical techniques described here include those used to obtain the emission data given in Appendix A and are those generally used in the sulfuric acid manufacturing industry. Format and wording for most of these procedures are those of the company that supplied the description.

## MODIFIED MONSANTO COMPANY TECHNIQUE FOR SAMPLING SULFURIC ACID MIST(*15*)

### Description of Sampling Equipment

The equipment used for sampling acid mist was constructed by the Public Health Service and is based on the equipment used by the Monsanto Company. This portable train allows collection of a wide range of mist or dust concentrations in a minimum of time. Particles greater than 3 microns diameter are determined separately from the smaller particles.

The Public Health Service sampling train, Figures B1 and B2, consists of a glass probe, a high-efficiency glass cyclone to collect particles larger than 3 microns diameter, and a filter that traps the smaller particles. A calibrated orifice, dry gas meter, and pump complete the train.

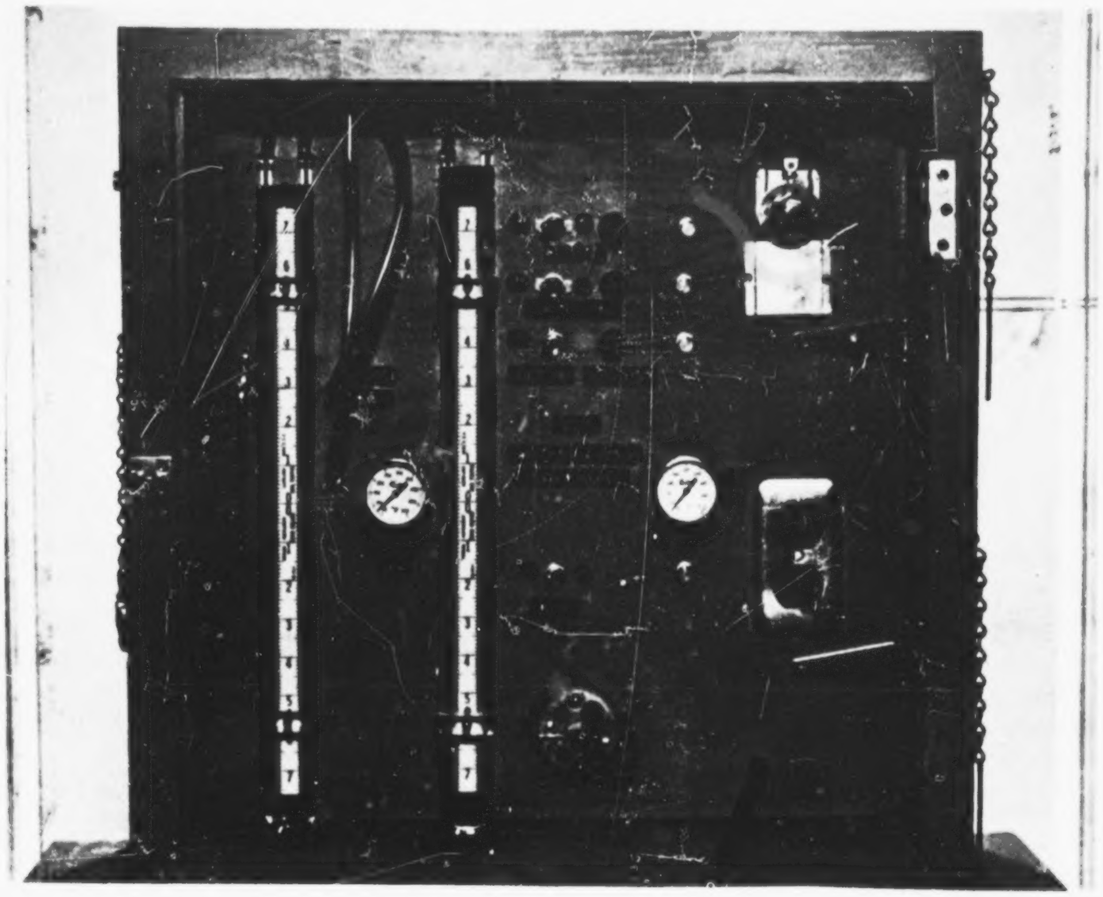

Figure B1 — Acid-mist sampling train, control panel.

To prevent condensation of mist in the train, the collection system is mounted in a heated, insulated box. Heating is accomplished by two thermostatically controlled electric heaters mounted in a transite box within the sampler. The heaters are rated at 1000 watts each at 110 volts. They consist of cone-shaped ceramic holders wound with heating wire and are commonly called bowl heaters. The transite box is open at each end, and a small fan circulates hot air around the collection equipment.

On the other side of the sampling box are mounted two manometers to indicate flow rate through the train, two dial stem thermometers to measure

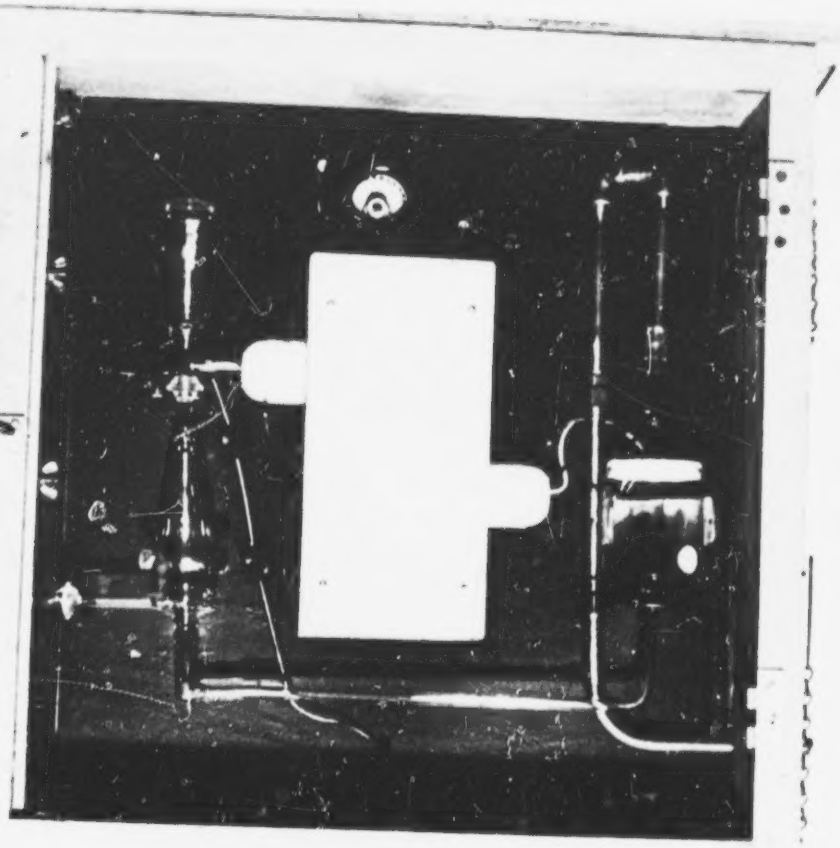

Figure B2 — Acid-mist sampling train, collection compartment.

temperatures at the cyclone and orifice, and a temperature-controlling thermostat.

The filter consists of a 65-mm-diameter glass Buchner funnel with a coarse-porosity filtering disc. Two layers of fiberglass filter paper (MSA CT 75428) are placed on the filtering disc to form the acid-mist filter. The packed fiberglass wool filter (Pyrex 3950) as described by Monsanto is also highly efficient

The dry gas meter may be omitted if the rate of flow through the calibrated orifice is carefully watched. In the field, however, circumstances may prevent careful observation of flow rate, and a dry gas meter insures accurate measurement of total volume flow.

## Selection of Sampling Points

The location and number of sampling points are based on size and shape of the duct, uniformity of gas flow in the duct, availability of sampling port, and space required to set up sampling equipment.

Straight vertical ducts with no flow obstructions for at least 8 diameters upstream of the sampling point are preferred. Sometimes one must settle for less than these ideal conditions.

To insure a representative sample of stack gas, the duct should be divided into a number of equal areas and sampled at the center of each of these areas.

The number of areas depends on the size of the stack. This procedure prevents erroneous results due to stratification of the acid mist in the duct. Bulletin WP-50 of the Western Precipitation Company may prove useful in determining the number of areas.

**Stack Gas Velocity**

The pitot tube is used for most velocity measurements. The basic equation for calculating velocity is, $V_s = 174K \sqrt{HT_s \times \frac{29.9}{P_s} \times \frac{29.0}{MW}}$, where $V_s$ is the gas velocity in feet per minute, K is the pitot tube calibration factor, H is the velocity head in inches of water, $T_s$ is the stack gas temperature in °R, $P_s$ is the absolute pressure of stack gas in inches of mercury, and MW is the molecular weight of the process gas. This equation simplifies to $V_s = 174K\sqrt{HT_s}$ when the stack pressure is approximately equal to 29.9 and the molecular weight of the process gas is equal to that of air (29.0).

**Determination of Sampling Rate**

In use of the acid mist train, a sampling rate of about 1 cfm at 70°F must be maintained in order to insure separation of particles larger than 3 microns diameter in the cyclone.

Nozzle area is then determined by dividing sampling rate by stack gas velocity, i.e. $A_n = \frac{\text{Q, sampling rate at stack gas conditions}}{V_s\text{, stack gas velocity}}$

It is, of course, impractical to vary nozzle size once sampling has begun. Therefore, if gas velocity varies considerably, the sampling rate must be varied and either cyclone efficiency or isokinetic sampling must be sacrificed. Isokinetic sampling is not necessary if previous testing has shown that about 90 percent of the acid mist particles are below 3 to 5 microns diameter.

Sampling rates and the corresponding pressure drop across the orifice should be computed for each sampling point before sampling is begun. These values should be recorded on the data sheet, Figure B3. Care must be taken in using the orifice calibration curve at various temperatures and pressures. A typical orifice calibration curve is shown in Figure B4. The following equations may prove useful:

$$\Delta P_o = \Delta P_{(calib)} \times \frac{530}{T_o} \times \frac{P_b - P_o}{29.9} \times \frac{MW}{29.0}$$

$$Q_o = Q_{(calib)} \times \frac{T_o}{530} \times \frac{29.9}{P_b - P_o}$$

$\Delta P_o$ = pressure drop across orifice at orifice pressure and temperature, in. $H_2O$

$P_b$ = barometric pressure, in. Hg

$\Delta P_{(calib)}$ = pressure drop across orifice at orifice calibration conditions, in. $H_2O$

$T_o$ = temperature at orifice, °R

$P_o$ = gauge pressure at inlet to orifice, in. Hg

MW = molecular weight of gas

$Q_o$ = flow through orifice at orifice temperature and pressure, cfm

$Q_{(calib)}$ = flow through orifice at calibration conditions, cfm

Date ______

Plant ______

Test No. ______

Location ______

$P_b$ = ______

| | | ORIFICE DATA* | | | | METER DATA | | |
|---|---|---|---|---|---|---|---|---|
| Position | Time, min. | Desired Flow ($A_n$ x $V_s$), cfm | ($\Delta P_o$), in. $H_2O$ | ($T_o$), °F | ($P_o$), in. Hg | Reading ($Q_m$), $ft^3$ | ($P_m$), in. Hg | ($T_m$), °F |
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*At stack conditions

$$\Delta P_o = \Delta P_{(calib)} \left( \frac{530}{460+T_o} \times \frac{P_b\text{-}P_o}{29.9} \times \frac{MW}{29.0} \right) =$$

$$Q_s = \text{Volume sampled in scf} = Q_m \times \frac{530}{460+T_m} \times \frac{P_b\text{-}P_m}{29.9} =$$

| | TITRATIONS cc of NaOH,N= | mg $H_2SO_4$ = cc x N x 49 | CONCENTRATION, mg/$ft^3$ |
|---|---|---|---|
| CYCLONE | | | |
| FIBER FILTER | | | |
| TOTAL | | | |

Figure B3 — Data sheet for sampling sulfuric acid mist.

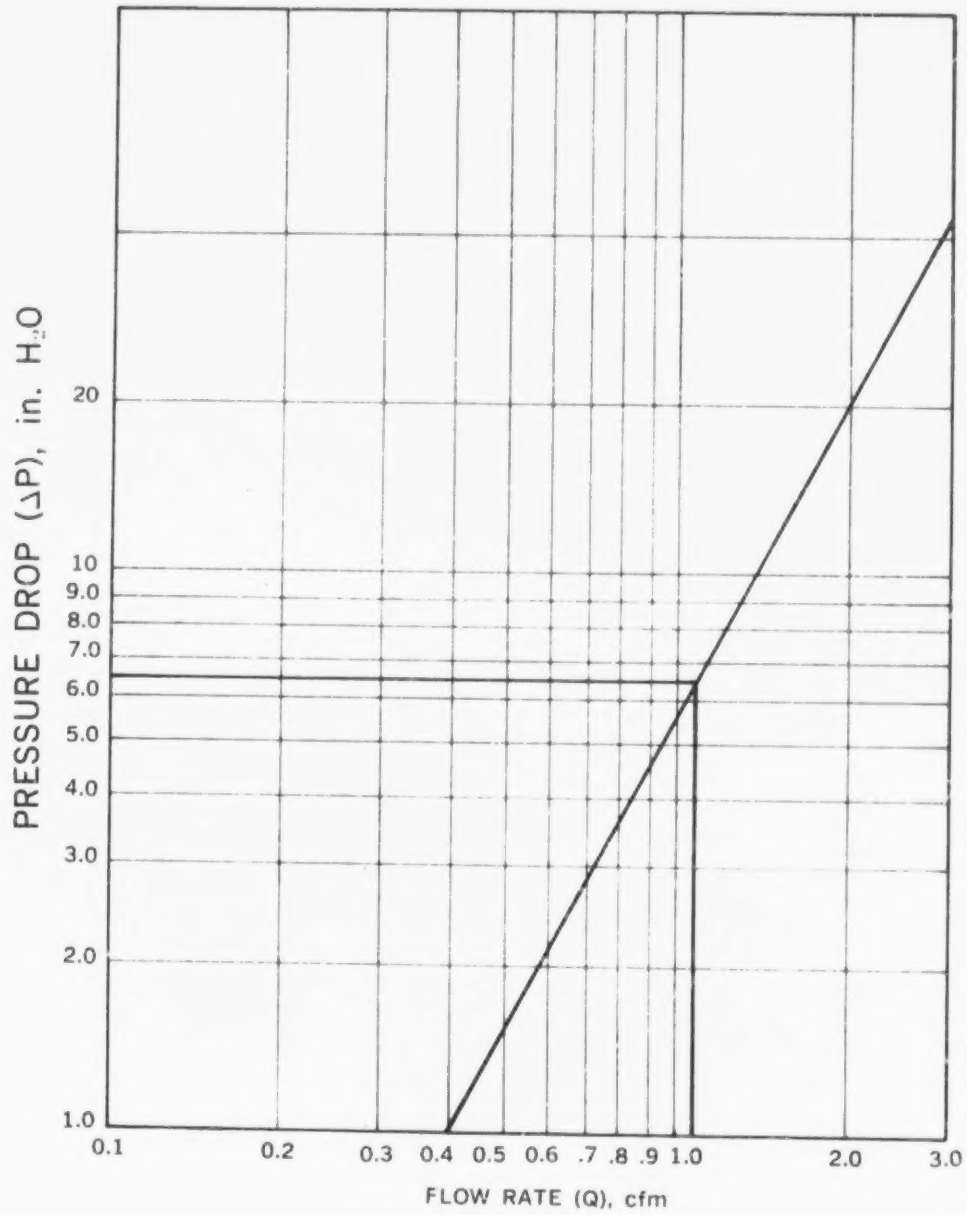


Figure B4 — Typical orifice calibration curve at 70°F and 29.9 in. Hg.

A sample calculation illustrates the procedure. Assume $T_o = 100°F$, $P_o = 2$ in. Hg, MW = 29.0, and $P_b = 29.9$ in. Hg. Desired sampling rate at 70°F is 1 $ft^3/min$ or 1.05 $ft^3/min$ at 100°F (the stack temperature). Stack velocity measured by pitot tube measurements was 1350 ft/min. The sample nozzle area is then equal to $\frac{1.05\ ft^3/min}{1350\ ft/min} = 0.778 \times 10^{-3}\ ft^2$. The area of the probe selected was $0.8 \times 10^{-3}\ ft^2$.

The required flow at the sampling point is the stack velocity times the probe area or $1350\ ft/min \times 0.8 \times 10^{-3}\ ft^2 = 1.08\ ft^3/min$ at stack temperature and pressure.

The corresponding orifice pressure drop at this flow is obtained by (1) entering the orifice calibration chart at the desired gas volume and reading the orifice pressure drop and (2) converting this pressure drop to conditions under which the orifice will operate.

For example,

1. Enter chart at 1.08 cfm and read $\Delta P = 6.5$ in. at calibration conditions.
2. $\Delta P_o = 6.5 \text{ in.} \times \frac{530}{560} \times \frac{29.9-2}{29.9} \times \frac{29.0}{29.0} = 5.74$ in. at orifice conditions.

Desired orifice setting is then 5.74 in. at this sampling point.

## Sample Collection

Place two thicknesses of fiberglass filter paper in the glass filter holder or firmly pack filter tube with glass wool to a depth of 2 inches, depending on which type of filtering system is used. Check the packing by drawing air through the train at about 1 cfm. A pressure drop of about 3 in. Hg indicates sufficient fiber wool packing.

Pressure check the train by plugging the probe and drawing a vacuum of 6 in. Hg. Close the line leading from the train; the vacuum should remain at 6 in. Hg if the train is leakproof. *Slowly* remove plug from probe to release vacuum and open line leading from train.

Close insulated door on sampling train and heat collection apparatus to 10°F above stack temperature. *Blower should be ON* whenever box is hot. Regulate temperature with the thermostat on front of box.

Heat probe by wrapping it with electrical heating tape over its entire exposed length.

When sample box reaches operating temperature, sampling can begin. During testing, record all pertinent data on the data sheet. Compute the desired flow and the corresponding pressure drop before sampling begins.

Normally a sample collection period of 20 to 30 minutes at a sampling rate of approximately 1 cfm should be sufficient. If expected acid-mist loadings are high, i.e. 50 mg per scf, it is possible to overload the glass filter media regardless of which type is used. In any case, the glass tubing downstream of the filter should be inspected often. Any carryover of acid mist will be indicated by droplets or liquid in the tubing.

## Sample Analysis

When sampling is completed, allow train to cool. Remove collected sample from probe and cyclone by rinsing with distilled water and collecting washings in a 500-ml beaker. Add five drops of phenolphthalein indicator solution and titrate with a standardized NaOH solution. For lower acid mist loadings of 0.5 to 50 mg/scf, use an NaOH solution of about 0.01 to 0.1N. For higher loadings, use a normality of about 1.0.

Remove the filter paper or glass wool from its holder and place in a beaker. Rinse the cyclone outlet line and the glass filter holder with distilled water and add this washing to the beaker with the filter. Add enough distilled water to thoroughly remove all of the acid mist from the filter and form a slurry. Stir the solution of paper or glass wool and water vigorously for 15 to 20 minutes to insure a uniform mixture. Vigorous stirring should also be employed during the titration with NaOH solution to determine an accurate end point. When glass wool is used as a filtering medium, a stainless steel stirring rod is recommended for stirring the rather thick, fluffy mixture of glass wool and water; many glass rods have been broken.

There are 49 mg $H_2SO_4$ per cc of 1.0N NaOH solution. Therefore, (cc NaOH) (N NaOH) (49) = mg $H_2SO_4$.

Take duplicate samples. Run blank titration with the filter medium used, because NaOH may be needed to neutralize the medium.

## MONSANTO COMPANY PROCEDURES FOR CONTACT SULFURIC ACID PLANTS

**Reich Test for Sulfur Dioxide** (Not for use in air-quench plants)

Entrance Gas Test — Flush the sample line thoroughly with gas before the test to insure getting a sample representative of operation at the time that the test is being made.

Fill the shaker bottle approximately two-thirds full of water and add about 5 ml of starch solution. Add 10 ml of N/10 iodine to the bottle by pipette, after first bringing the solution to a *faint* blue color by adding one or two drops of iodine solution. It is preferable to use the same water with starch indicator in the shaker bottle for a number of determinations. Either acidify new water in the shaker bottle with two drops of acid or repeat the first determination to obtain a good reading.

With all clamps and stopcocks closed, place the rubber stopper in the test bottle. Adjust the water level in a 250-cc burette to the "zero mark" by raising the water bottle with the glass stopcocks at the top and bottom of the burette open. Then close the top stopcock and place the water bottle back on the table. *Make sure that all connections in the apparatus are tight.*

Open the clamp on the sampling tube, adjusting it so that the gas bubbles pass *slowly* through the solution in the bottle. Shake the bottle continuously when gas is bubbling in to insure complete absorption of $SO_2$. Continue until the solution has changed to the same *faint* blue color obtained previously. Be careful not to overrun the end point.

Close the clamp on the sampling line tightly when the end point has been reached. Raise the water bottle so that its water level is balanced against the water level in the burette, and then note the amount of air that has been displaced in the burette. Note the temperature on the thermometer. Values for entrance gas are given in Table B1; refer to the column headed by the temperature nearest that noted during the test. Follow down this column to find the number nearest to the measured volume of air in the cylinder. Then read the corresponding percent $SO_2$ from the table. For example, if the temperature is 30°C and the measured volume is 145 ml, then the strength of the gas is 8.0 percent.

Exit Gas Test — Leave the water aspirator that maintains suction on the exit gas sampling line running at all times to insure a representative sample of gas. If gas is flowing through the line, a slight suction will show on the manometer.

Now, in the exit gas test apparatus, repeat the procedure used for the entrance gas test except use 10 ml of N/100 iodine solution instead of N/10 iodine solution. Note the volume of air displaced and the temperature as before, then refer to the exit gas values in Table B2 for the percent $SO_2$. Barometric correction factors are given in Table B3; normal barometer readings for various altitudes, in Table B4.

Conversion Efficiency — Refer to Table B5 for the percentage conversion efficiency. For example, if the entrance gas is 8.0 percent and the exit gas is 0.22 percent, the conversion efficiency is [illegible] percent.

Solutions — The solution of N/100 iodine solution may be prepared with sufficient accuracy by measuring 100 ml of the standardized N/10 iodine

## TABLE B1. REICH TEST FOR $SO_2$ IN ENTRANCE GAS

(Solution: 10 cc $\frac{N}{10}$ I)

Gas volume, ml, at indicated temperature, °C

| °C<br>% $SO_2$ | 5° | 10° | 15° | 20° | 25° | 30° | 35° | 40° |
|---|---|---|---|---|---|---|---|---|
| 1.0 | 1112 | 1137 | 1162 | 1190 | 1221 | 1255 | 1294 | 1340 |
| 1.2 | 925 | 945 | 967 | 990 | 1015 | 1043 | 1076 | 1114 |
| 1.4 | 791 | 808 | 827 | 846 | 868 | 892 | 921 | 953 |
| 1.6 | 691 | 706 | 722 | 739 | 758 | 779 | 804 | 832 |
| 1.8 | 613 | 626 | 640 | 656 | 673 | 691 | 713 | 738 |
| 2.0 | 550 | 562 | 575 | 589 | 604 | 621 | 640 | 663 |
| 2.2 | 499 | 510 | 522 | 534 | 548 | 563 | 581 | 601 |
| 2.4 | 457 | 467 | 477 | 489 | 501 | 515 | 531 | 550 |
| 2.6 | 421 | 430 | 440 | 450 | 462 | 474 | 489 | 507 |
| 2.8 | 390 | 398 | 407 | 417 | 428 | 440 | 453 | 469 |
| 3.0 | 363 | 371 | 379 | 388 | 398 | 409 | 422 | 437 |
| 3.2 | 340 | 347 | 355 | 363 | 373 | 383 | 395 | 409 |
| 3.4 | 319 | 326 | 333 | 341 | 350 | 360 | 371 | 384 |
| 3.6 | 300 | 307 | 314 | 322 | 330 | 339 | 350 | 362 |
| 3.8 | 284 | 290 | 297 | 304 | 312 | 320 | 331 | 342 |
| 4.0 | 269 | 275 | 281 | 288 | 296 | 304 | 313 | 324 |
| 4.2 | 256 | 261 | 267 | 274 | 281 | 289 | 298 | 308 |
| 4.4 | 244 | 249 | 255 | 261 | 267 | 275 | 284 | 294 |
| 4.6 | 233 | 238 | 243 | 249 | 255 | 262 | 271 | 280 |
| 4.8 | 222 | 228 | 232 | 238 | 244 | 251 | 259 | 268 |
| 5.0 | 213 | 218 | 223 | 228 | 234 | 240 | 248 | 257 |
| 5.2 | 204 | 209 | 214 | 219 | 224 | 231 | 238 | 246 |
| 5.4 | 196 | 201 | 205 | 210 | 216 | 222 | 229 | 237 |
| 5.6 | 189 | 193 | 197 | 202 | 207 | 213 | 220 | 228 |
| 5.8 | 182 | 186 | 190 | 195 | 200 | 205 | 212 | 219 |
| 6.0 | 176 | 179 | 183 | 188 | 193 | 198 | 204 | 212 |
| 6.2 | 170 | 173 | 177 | 181 | 186 | 191 | 197 | 204 |
| 6.4 | 164 | 167 | 171 | 175 | 180 | 185 | 191 | 197 |
| 6.6 | 159 | 162 | 166 | 170 | 174 | 179 | 185 | 191 |
| 6.8 | 154 | 157 | 160 | 164 | 169 | 173 | 179 | 185 |
| 7.0 | 148 | 152 | 155 | 159 | 163 | 168 | 173 | 179 |
| 7.2 | 145 | 148 | 151 | 154 | 158 | 163 | 168 | 174 |
| 7.4 | 141 | 143 | 146 | 150 | 154 | 158 | 163 | 169 |
| 7.6 | 137 | 139 | 142 | 146 | 149 | 154 | 158 | 164 |

TABLE B1 (Continued)

Gas volume, ml, at indicated temperature, °C

| °C<br>% $SO_2$ | 5° | 10° | 15° | 20° | 25° | 30° | 35° | 40° |
|---|---|---|---|---|---|---|---|---|
| 7.8 | 133 | 135 | 138 | 142 | 145 | 149 | 154 | 160 |
| 8.0 | 129 | 132 | 135 | 138 | 141 | 145 | 150 | 155 |
| 8.2 | 126 | 129 | 131 | 134 | 138 | 141 | 146 | 151 |
| 8.4 | 123 | 125 | 128 | 131 | 135 | 138 | 142 | 148 |
| 8.6 | 120 | 122 | 125 | 128 | 131 | 134 | 138 | 144 |
| 8.8 | 117 | 119 | 122 | 125 | 128 | 131 | 136 | 140 |
| 9.0 | 114 | 116 | 119 | 122 | 125 | 128 | 132 | 137 |
| 9.2 | 111 | 113 | 116 | 119 | 122 | 125 | 129 | 134 |
| 9.4 | 108 | 111 | 113 | 116 | 119 | 122 | 126 | 130 |
| 9.6 | 106 | 108 | 111 | 113 | 116 | 119 | 123 | 127 |
| 9.8 | 103 | 106 | 108 | 111 | 114 | 117 | 120 | 130 |
| 10.0 | 101 | 103 | 105 | 108 | 111 | 114 | 118 | 122 |
| 10.2 | 99 | 101 | 103 | 106 | 109 | 112 | 115 | 119 |
| 10.4 | 97 | 99 | 101 | 104 | 106 | 109 | 113 | 117 |
| 10.6 | 95 | 97 | 99 | 101 | 104 | 107 | 110 | 114 |
| 10.8 | 93 | 95 | 97 | 99 | 102 | 105 | 108 | 112 |
| 11.0 | 91 | 93 | 95 | 97 | 100 | 103 | 106 | 110 |
| 11.2 | 89 | 91 | 93 | 95 | 98 | 101 | 104 | 107 |
| 11.4 | 87 | 89 | 91 | 93 | 96 | 99 | 102 | 105 |
| 11.6 | 86 | 88 | 90 | 92 | 94 | 97 | 100 | 103 |
| 11.8 | 84 | 86 | 88 | 90 | 92 | 95 | 98 | 101 |

Formula used in making calculations:

$$x = \frac{1094.4}{C\left(\frac{B - W}{760\ (1 + 0.00366t)}\right) + 10.944}$$

where B = barometric pressure, mm Hg
C = gas collected, cc
t = temperature of gas, °C
W = aqueous vapor pressure at temperature t, mm Hg
x = $SO_2$ in gas, %

Percentages of $SO_2$ not listed in the table may be calculated by use of the factor (K), given in Table B3, in this formula:

$$x = \frac{1094.4}{CK + 10.944} \qquad \left(\text{for 10 cc } \frac{N}{10}\ I\right)$$

Where more accurate results are desired for the value of (K) than to the nearest 10 mm Hg and the nearest 5°C, interpolate in Table B3.

The values in Table B1 are calculated for a barometric pressure of 760 mm Hg. See Table B3 for corrections for other pressures.

## TABLE B2. REICH TEST FOR $SO_2$ IN EXIT GAS

(Solution: $10\ \text{cc}\ \frac{N}{100}\ I$)

| | Gas volume, ml, at indicated temperature, °C | | | | | | | |
|---|---|---|---|---|---|---|---|---|
| °C<br>% $SO_2$ | 5° | 10° | 15° | 20° | 25° | 30° | 35° | 40° |
| 0.05 | 2245 | 2297 | 2347 | 2403 | 2460 | 2537 | 2616 | 2707 |
| 0.10 | 1123 | 1147 | 1172 | 1201 | 1232 | 1266 | 1307 | 1353 |
| 0.11 | 1021 | 1043 | 1067 | 1092 | 1120 | 1152 | 1188 | 1229 |
| 0.12 | 936 | 956 | 978 | 1001 | 1026 | 1055 | 1088 | 1127 |
| 0.13 | 863 | 882 | 903 | 924 | 948 | 974 | 1004 | 1040 |
| 0.14 | 802 | 819 | 838 | 858 | 880 | 904 | 932 | 965 |
| 0.15 | 748 | 764 | 781 | 800 | 820 | 844 | 870 | 901 |
| 0.16 | 700 | 713 | 733 | 753 | 769 | 792 | 815 | 847 |
| 0.17 | 658 | 673 | 692 | 705 | 723 | 743 | 770 | 798 |
| 0.18 | 624 | 636 | 650 | 666 | 683 | 705 | 724 | 749 |
| 0.19 | 591 | 603 | 617 | 631 | 647 | 666 | 688 | 710 |
| 0.20 | 560 | 573 | 586 | 600 | 615 | 632 | 652 | 675 |
| 0.22 | 511 | 520 | 533 | 547 | 561 | 575 | 594 | 613 |
| 0.24 | 467 | 477 | 488 | 501 | 513 | 528 | 543 | 563 |
| 0.25 | 448 | 458 | 468 | 479 | 492 | 505 | 521 | 540 |
| 0.26 | 431 | 440 | 451 | 463 | 473 | 488 | 501 | 520 |
| 0.28 | 400 | 408 | 418 | 428 | 440 | 451 | 467 | 483 |
| 0.30 | 373 | 381 | 390 | 399 | 409 | 421 | 434 | 449 |
| 0.32 | 350 | 358 | 366 | 375 | 384 | 395 | 407 | 421 |
| 0.34 | 330 | 337 | 345 | 353 | 362 | 372 | 384 | 397 |
| 0.35 | 320 | 327 | 334 | 342 | 351 | 361 | 372 | 385 |
| 0.36 | 311 | 318 | 326 | 334 | 342 | 352 | 363 | 375 |
| 0.38 | 295 | 302 | 308 | 315 | 324 | 332 | 343 | 355 |
| 0.40 | 279 | 286 | 292 | 299 | 307 | 315 | 325 | 337 |
| 0.45 | 248 | 254 | 259 | 266 | 272 | 280 | 284 | 299 |
| 0.50 | 223 | 228 | 233 | 239 | 245 | 252 | 260 | 269 |
| 0.55 | 203 | 207 | 212 | 217 | 223 | 229 | 236 | 244 |
| 0.60 | 186 | 190 | 194 | 199 | 204 | 210 | 216 | 224 |
| 0.65 | 171 | 175 | 179 | 183 | 188 | 193 | 199 | 206 |
| 0.70 | 159 | 162 | 166 | 170 | 174 | 179 | 185 | 192 |
| 0.75 | 148 | 152 | 155 | 159 | 163 | 167 | 173 | 179 |
| 0.80 | 139 | 142 | 145 | 149 | 152 | 157 | 162 | 167 |
| 0.85 | 131 | 133 | 137 | 140 | 143 | 147 | 152 | 157 |
| 0.90 | 123 | 126 | 129 | 132 | 135 | 139 | 143 | 149 |
| 0.95 | 117 | 119 | 122 | 125 | 128 | 132 | 136 | 141 |
| 1.00 | 111 | 113 | 116 | 119 | 122 | 125 | 129 | 134 |

TABLE B2 (Continued)

Formula used in making calculations:

$$x = \frac{109.44}{C\left(\frac{B - W}{760\ (1 + 0.00366t)}\right) + 1.0944}$$

where B = barometric pressure, mm Hg
C = gas collected, cc
t = temperature of gas, °C
W = aqueous vapor pressure at temperature t, mm Hg
x = $SO_2$ in gas, %

Percentages of $SO_2$ not listed in the table may be calculated by use of the factor (K), given in Table B3, in this formula:

$$x = \frac{109.44}{CK + 1.0944} \quad (\text{for } 10 \text{ cc } \frac{N}{100} \text{ I})$$

Where more accurate results are desired for the value of (k) than to the nearest 10 mm Hg and the nearest 5°C, interpolate in Table B3.

The values in Table B2 are calculated for a barometric pressure of 760 mm Hg. See Table B3 for corrections for other pressures.

## TABLE B3. BAROMETRIC CORRECTION FACTORS FOR REICH TEST

| Pressure mm Hg | Temperature, C° | | | | | | | |
|---|---|---|---|---|---|---|---|---|
| | 5° | 10° | 15° | 20° | 25° | 30° | 35° | 40° |
| 760 | 0.974 | 0.953 | 0.932 | 0.910 | 0.887 | 0.863 | 0.837 | 0.809 |
| 750 | 0.961 | 0.940 | 0.919 | 0.898 | 0.875 | 0.851 | 0.825 | 0.797 |
| 740 | 0.958 | 0.928 | 0.907 | 0.886 | 0.863 | 0.840 | 0.814 | 0.786 |
| 730 | 0.935 | 0.915 | 0.895 | 0.873 | 0.851 | 0.828 | 0.802 | 0.774 |
| 720 | 0.922 | 0.902 | 0.882 | 0.861 | 0.839 | 0.816 | 0.790 | 0.763 |
| 710 | 0.909 | 0.890 | 0.870 | 0.849 | 0.827 | 0.804 | 0.779 | 0.751 |
| 700 | 0.897 | 0.877 | 0.857 | 0.837 | 0.815 | 0.792 | 0.767 | 0.740 |
| 690 | 0.882 | 0.864 | 0.845 | 0.825 | 0.803 | 0.780 | 0.756 | 0.728 |
| 680 | 0.870 | 0.852 | 0.832 | 0.812 | 0.791 | 0.769 | 0.744 | 0.717 |
| 670 | 0.857 | 0.839 | 0.820 | 0.800 | 0.779 | 0.757 | 0.732 | 0.706 |
| 660 | 0.844 | 0.826 | 0.807 | 0.788 | 0.767 | 0.745 | 0.721 | 0.694 |
| 650 | 0.832 | 0.813 | 0.795 | 0.775 | 0.755 | 0.733 | 0.709 | 0.683 |
| 640 | 0.819 | 0.801 | 0.782 | 0.763 | 0.743 | 0.721 | 0.697 | 0.671 |
| 630 | 0.806 | 0.788 | 0.770 | 0.751 | 0.731 | 0.709 | 0.686 | 0.660 |
| 620 | 0.793 | 0.775 | 0.757 | 0.739 | 0.719 | 0.697 | 0.674 | 0.648 |
| 610 | 0.776 | 0.762 | 0.745 | 0.726 | 0.707 | 0.686 | 0.662 | 0.637 |
| 600 | 0.767 | 0.750 | 0.732 | 0.714 | 0.695 | 0.674 | 0.651 | 0.625 |
| 590 | 0.754 | 0.737 | 0.720 | 0.702 | 0.683 | 0.662 | 0.639 | 0.614 |
| 580 | 0.741 | 0.725 | 0.707 | 0.690 | 0.670 | 0.650 | 0.627 | 0.602 |
| 570 | 0.728 | 0.712 | 0.695 | 0.677 | 0.658 | 0.638 | 0.616 | 0.591 |
| 560 | 0.715 | 0.699 | 0.683 | 0.665 | 0.646 | 0.626 | 0.604 | 0.579 |
| 550 | 0.702 | 0.686 | 0.670 | 0.653 | 0.634 | 0.614 | 0.592 | 0.568 |
| 540 | 0.689 | 0.674 | 0.658 | 0.641 | 0.622 | 0.603 | 0.581 | 0.556 |
| 530 | 0.676 | 0.661 | 0.645 | 0.628 | 0.610 | 0.591 | 0.569 | 0.545 |
| 520 | 0.664 | 0.648 | 0.633 | 0.616 | 0.598 | 0.579 | 0.557 | 0.533 |
| 510 | 0.651 | 0.636 | 0.620 | 0.604 | 0.586 | 0.567 | 0.546 | 0.522 |

Entrance gas and exit gas values shown in Tables B1 and B2 were calculated for a barometric pressure of 760 mm Hg. If a correction for barometric pressure is desired, find the factor (K) in Table B3 that corresponds to the temperature and barometric pressure of the test under consideration and determine a corrected temperature by multiplying the factor (K) by the temperature of the test under consideration. Then use Table B1 or B2, applying this corrected temperature in place of the test temperature.

## TABLE B4. NORMAL BAROMETER READINGS FOR VARIOUS ALTITUDES

| Altitude, feet | Pressure, mm Hg |
|---|---|
| 0 | 760 |
| 500 | 746 |
| 1000 | 733 |
| 1500 | 720 |
| 2000 | 707 |
| 2500 | 694 |
| 3000 | 681 |
| 3500 | 669 |
| 4000 | 656 |
| 4500 | 644 |
| 5000 | 632 |
| 5500 | 621 |
| 6000 | 609 |
| 6500 | 598 |
| 7000 | 586 |
| 7500 | 575 |
| 8000 | 564 |
| 8500 | 554 |
| 9000 | 543 |
| 9500 | 533 |
| 10000 | 523 |

## TABLE B5. $SO_2$ CONVERSION CHART FOR SULFUR-BURNING PLANTS WITH NO AIR QUENCH

| $SO_2$ in entrance gas, % | Percentage of $SO_2$ converted to $SO_3$ | | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | $SO_2$ in exit gas | | | | | | | | | | | |
| | 0.05 | 0.10 | 0.12 | 0.14 | 0.16 | 0.18 | 0.20 | 0.22 | 0.24 | 0.26 | 0.28 | 0.30 |
| 3.5 | 98.8 | 97.4 | 97.0 | 96.5 | 96.1 | 95.5 | 94.7 | 94.2 | 93.6 | 93.2 | 92.6 | 92.0 |
| 4.0 | 98.9 | 97.7 | 97.3 | 96.8 | 96.4 | 95.9 | 95.3 | 94.8 | 94.3 | 93.9 | 93.4 | 92.9 |
| 4.2 | 98.9 | 97.8 | 97.4 | 96.9 | 96.6 | 96.1 | 95.5 | 95.1 | 94.6 | 94.2 | 93.8 | 93.3 |
| 4.4 | 99.0 | 97.9 | 97.5 | 97.0 | 96.7 | 96.3 | 95.7 | 95.3 | 94.9 | 94.5 | 94.1 | 93.6 |
| 4.6 | 99.0 | 98.0 | 97.6 | 97.2 | 96.8 | 96.4 | 95.9 | 95.5 | 95.1 | 94.7 | 94.3 | 93.9 |
| 4.8 | 99.1 | 98.1 | 97.7 | 97.3 | 96.9 | 96.6 | 96.1 | 95.7 | 95.2 | 94.8 | 94.5 | 94.2 |
| 5.0 | 99.1 | 98.2 | 97.8 | 97.4 | 97.0 | 96.7 | 96.3 | 95.9 | 95.5 | 95.1 | 94.7 | 94.4 |
| 5.2 | 99.1 | 98.2 | 97.9 | 97.4 | 97.1 | 96.7 | 96.4 | 96.1 | 95.7 | 95.3 | 95.0 | 94.7 |
| 5.4 | 99.2 | 98.3 | 97.9 | 97.5 | 97.3 | 96.9 | 96.6 | 96.3 | 95.9 | 95.5 | 95.2 | 94.9 |
| 5.6 | 99.2 | 98.4 | 98.0 | 97.6 | 97.4 | 97.0 | 96.7 | 96.4 | 96.1 | 95.7 | 95.4 | 95.1 |
| 5.8 | 99.2 | 98.4 | 98.0 | 97.7 | 97.5 | 97.2 | 96.9 | 96.6 | 96.3 | 95.9 | 95.6 | 95.3 |
| 6.0 | 99.3 | 98.5 | 98.1 | 97.8 | 97.6 | 97.4 | 97.0 | 96.7 | 96.4 | 96.0 | 95.7 | 95.4 |
| 6.2 | 99.3 | 98.5 | 98.2 | 97.9 | 97.7 | 97.4 | 97.1 | 96.9 | 96.5 | 96.1 | 95.9 | 95.6 |
| 6.4 | 99.3 | 98.6 | 98.2 | 98.0 | 97.8 | 97.5 | 97.2 | 97.0 | 96.7 | 96.3 | 96.1 | 95.8 |
| 6.6 | 99.3 | 98.6 | 98.3 | 98.1 | 97.9 | 97.6 | 97.3 | 97.1 | 96.8 | 96.4 | 96.2 | 95.9 |
| 6.8 | 99.3 | 98.7 | 98.4 | 98.1 | 97.9 | 97.6 | 97.4 | 97.2 | 96.9 | 96.5 | 96.2 | 96.0 |
| 7.0 | 99.4 | 98.7 | 98.4 | 98.2 | 98.0 | 97.8 | 97.4 | 97.2 | 97.0 | 96.6 | 96.4 | 96.2 |
| 7.2 | 99.4 | 98.8 | 98.5 | 98.2 | 98.0 | 97.8 | 97.5 | 97.3 | 97.0 | 96.7 | 96.5 | 96.3 |
| 7.4 | 99.4 | 98.8 | 98.5 | 98.3 | 98.1 | 97.9 | 97.6 | 97.4 | 97.1 | 96.8 | 96.6 | 96.4 |
| 7.6 | 99.4 | 98.8 | 98.6 | 98.4 | 98.2 | 98.0 | 97.7 | 97.5 | 97.2 | 96.9 | 96.7 | 96.5 |
| 7.8 | 99.5 | 98.9 | 98.6 | 98.4 | 98.2 | 98.0 | 97.7 | 97.5 | 97.3 | 97.0 | 96.8 | 96.6 |
| 8.0 | 99.5 | 98.9 | 98.7 | 98.5 | 98.2 | 98.0 | 97.8 | 97.6 | 97.4 | 97.1 | 96.9 | 96.7 |
| 8.2 | 99.5 | 98.9 | 98.7 | 98.5 | 98.3 | 98.1 | 97.9 | 97.7 | 97.4 | 97.2 | 97.0 | 96.8 |
| 8.4 | 99.5 | 99.0 | 98.7 | 98.5 | 98.3 | 98.1 | 97.9 | 97.7 | 97.5 | 97.3 | 97.1 | 96.9 |
| 8.6 | 99.5 | 99.0 | 98.8 | 98.6 | 98.4 | 98.2 | 98.0 | 97.8 | 97.5 | 97.4 | 97.2 | 97.0 |
| 8.8 | 99.5 | 99.0 | 98.8 | 98.6 | 98.4 | 98.2 | 98.0 | 97.8 | 97.6 | 97.4 | 97.2 | 97.0 |
| 9.0 | 99.5 | 99.0 | 98.8 | 98.6 | 98.5 | 98.3 | 98.1 | 97.9 | 97.7 | 97.5 | 97.3 | 97.1 |
| 9.2 | 99.5 | 99.1 | 98.8 | 98.7 | 98.5 | 98.3 | 98.1 | 97.9 | 97.7 | 97.5 | 97.4 | 97.2 |
| 9.4 | 99.6 | 99.1 | 98.9 | 98.7 | 98.5 | 98.3 | 98.2 | 98.0 | 97.8 | 97.6 | 97.4 | 97.2 |
| 9.6 | 99.6 | 99.1 | 98.9 | 98.7 | 98.6 | 98.4 | 98.2 | 98.1 | 97.9 | 97.7 | 97.5 | 97.3 |
| 9.8 | 99.6 | 99.1 | 98.9 | 98.8 | 98.6 | 98.4 | 98.3 | 98.2 | 97.9 | 97.7 | 97.6 | 97.4 |
| 10.0 | 99.6 | 99.2 | 99.0 | 98.8 | 98.6 | 98.5 | 98.3 | 98.2 | 98.0 | 97.8 | 97.6 | 97.4 |
| 10.2 | 99.6 | 99.2 | 99.0 | 98.8 | 98.7 | 98.5 | 98.3 | 98.2 | 98.0 | 97.8 | 97.7 | 97.5 |
| 10.4 | 99.6 | 99.2 | 99.0 | 98.8 | 98.7 | 98.5 | 98.4 | 98.2 | 98.0 | 97.9 | 97.7 | 97.6 |
| 10.6 | 99.6 | 99.2 | 99.1 | 98.9 | 98.7 | 98.6 | 98.4 | 98.2 | 98.1 | 97.9 | 97.8 | 97.6 |
| 10.8 | 99.6 | 99.2 | 99.1 | 98.9 | 98.7 | 98.6 | 98.4 | 98.3 | 98.1 | 98.0 | 97.9 | 97.7 |
| 11.0 | 99.6 | 99.2 | 99.1 | 99.0 | 98.8 | 98.6 | 98.5 | 98.3 | 98.2 | 98.0 | 97.9 | 97.7 |
| 11.2 | 99.6 | 99.3 | 99.1 | 99.0 | 98.8 | 98.7 | 98.5 | 98.3 | 98.2 | 98.0 | 97.9 | 97.8 |
| 11.4 | 99.6 | 99.3 | 99.1 | 99.0 | 98.8 | 98.7 | 98.5 | 98.4 | 98.2 | 98.1 | 98.0 | 97.8 |
| 11.6 | 99.6 | 99.3 | 99.1 | 99.0 | 98.9 | 98.7 | 98.6 | 98.4 | 98.3 | 98.1 | 98.0 | 97.9 |
| 11.8 | 99.7 | 99.3 | 99.2 | 99.0 | 98.9 | 98.7 | 98.6 | 98.5 | 98.3 | 98.2 | 98.0 | 97.9 |

x = % conversion of $SO_2$ to $SO_3$

a = % $SO_2$ in entrance gas

TABLE B5 (Continued)

| $SO_2$ in entrance gas, % | Percentage of $SO_2$ converted to $SO_3$ | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|
| | $SO_2$ in exit gas | | | | | | | | | | |
| | 0.32 | 0.34 | 0.36 | 0.38 | 0.40 | 0.50 | 0.60 | 0.70 | 0.80 | 0.90 | 1.00 |
| 3.5 | 91.5 | 91.0 | 90.5 | 89.9 | 88.3 | 86.3 | 83.7 | 80.8 | 78.0 | 75.2 | 72.7 |
| 4.0 | 92.4 | 92.0 | 91.5 | 91.0 | 90.5 | 88.2 | 85.8 | 83.4 | 81.0 | 78.6 | 76.1 |
| 4.2 | 92.8 | 92.4 | 92.0 | 91.5 | 91.0 | 88.8 | 86.5 | 84.2 | 81.9 | 79.7 | 77.4 |
| 4.4 | 93.2 | 92.8 | 92.3 | 92.0 | 91.5 | 89.3 | 87.2 | 85.0 | 82.8 | 80.6 | 78.5 |
| 4.6 | 93.5 | 93.1 | 92.7 | 92.3 | 91.9 | 89.8 | 87.8 | 85.7 | 83.6 | 81.5 | 79.5 |
| 4.8 | 93.8 | 93.4 | 93.0 | 92.6 | 92.2 | 90.3 | 83.3 | 86.3 | 84.3 | 82.4 | 80.4 |
| 5.0 | 94.1 | 93.7 | 93.3 | 93.0 | 92.6 | 90.7 | 88.8 | 86.9 | 85.0 | 83.1 | 81.2 |
| 5.2 | 94.4 | 94.0 | 93.6 | 93.3 | 92.9 | 91.1 | 89.3 | 87.5 | 85.6 | 83.8 | 82.0 |
| 5.4 | 94.6 | 94.2 | 93.9 | 93.6 | 93.2 | 91.4 | 89.7 | 88.0 | 86.2 | 84.5 | 82.7 |
| 5.6 | 94.8 | 94.5 | 94.2 | 93.8 | 93.4 | 91.8 | 90.1 | 88.4 | 86.8 | 85.1 | 83.4 |
| 5.8 | 95.0 | 94.7 | 94.4 | 94.1 | 93.7 | 92.1 | 90.5 | 88.9 | 87.3 | 85.6 | 84.0 |
| 6.0 | 95.2 | 94.9 | 94.6 | 94.3 | 93.9 | 92.4 | 90.8 | 89.3 | 87.7 | 86.2 | 84.6 |
| 6.2 | 95.4 | 95.1 | 94.8 | 94.5 | 94.1 | 92.6 | 91.2 | 89.7 | 88.2 | 86.7 | 85.2 |
| 6.4 | 95.5 | 95.2 | 94.9 | 94.6 | 94.3 | 92.9 | 91.5 | 90.0 | 88.6 | 87.1 | 85.7 |
| 6.6 | 95.7 | 95.4 | 95.1 | 94.8 | 94.5 | 93.1 | 91.7 | 90.4 | 89.0 | 87.6 | 86.1 |
| 6.8 | 95.9 | 95.6 | 95.3 | 95.0 | 94.7 | 93.4 | 92.0 | 90.7 | 89.3 | 88.0 | 86.6 |
| 7.0 | 95.9 | 95.6 | 95.4 | 95.2 | 94.9 | 93.6 | 92.3 | 91.0 | 89.6 | 88.3 | 87.0 |
| 7.2 | 96.1 | 95.8 | 95.6 | 95.3 | 95.0 | 93.8 | 92.5 | 91.2 | 90.0 | 88.7 | 87.4 |
| 7.4 | 96.2 | 95.9 | 95.7 | 95.5 | 95.2 | 94.0 | 92.7 | 91.5 | 90.3 | 89.0 | 87.8 |
| 7.6 | 96.3 | 96.0 | 95.8 | 95.6 | 95.3 | 94.1 | 93.0 | 91.8 | 90.6 | 89.4 | 88.2 |
| 7.8 | 96.4 | 96.1 | 95.9 | 95.7 | 95.5 | 94.3 | 93.2 | 92.0 | 90.8 | 89.7 | 88.5 |
| 8.0 | 96.5 | 96.2 | 96.0 | 95.8 | 95.6 | 94.5 | 93.3 | 92.2 | 91.1 | 90.0 | 88.8 |
| 8.2 | 96.6 | 96.3 | 96.1 | 95.9 | 95.7 | 94.6 | 93.5 | 92.4 | 91.4 | 90.3 | 89.2 |
| 8.4 | 96.7 | 96.5 | 96.3 | 96.0 | 95.8 | 94.8 | 93.7 | 92.6 | 91.6 | 90.5 | 89.5 |
| 8.6 | 96.8 | 96.5 | 96.3 | 96.1 | 95.9 | 94.9 | 93.9 | 92.8 | 91.8 | 90.8 | 89.7 |
| 8.8 | 96.8 | 96.6 | 96.4 | 96.2 | 96.0 | 95.0 | 94.0 | 93.0 | 92.0 | 91.0 | 90.0 |
| 9.0 | 96.9 | 96.7 | 96.5 | 96.3 | 96.2 | 95.2 | 94.2 | 93.2 | 92.2 | 91.2 | 90.2 |
| 9.2 | 97.0 | 96.8 | 96.6 | 96.4 | 96.2 | 95.3 | 94.3 | 93.4 | 92.4 | 91.5 | 90.5 |
| 9.4 | 97.1 | 96.9 | 96.7 | 96.5 | 96.3 | 95.4 | 94.5 | 93.5 | 92.6 | 91.7 | 90.7 |
| 9.6 | 97.2 | 97.0 | 96.8 | 96.6 | 96.4 | 95.5 | 94.6 | 93.7 | 92.8 | 91.9 | 91.0 |
| 9.8 | 97.3 | 97.1 | 96.9 | 96.7 | 96.5 | 95.6 | 94.7 | 93.8 | 93.0 | 92.1 | 91.2 |
| 10.0 | 97.3 | 97.1 | 96.9 | 96.8 | 96.6 | 95.7 | 94.8 | 94.0 | 93.1 | 92.2 | 91.4 |
| 10.2 | 97.3 | 97.1 | 97.0 | 96.8 | 96.7 | 95.8 | 95.0 | 94.1 | 93.3 | 92.4 | 91.6 |
| 10.4 | 97.4 | 97.2 | 97.1 | 96.9 | 96.7 | 95.9 | 95.1 | 94.3 | 93.4 | 92.6 | 91.8 |
| 10.6 | 97.4 | 97.3 | 97.1 | 97.0 | 96.8 | 96.0 | 95.2 | 94.4 | 93.6 | 92.7 | 91.9 |
| 10.8 | 97.5 | 97.3 | 97.2 | 97.0 | 96.9 | 96.1 | 95.3 | 94.5 | 93.7 | 92.9 | 92.1 |
| 11.0 | 97.6 | 97.4 | 97.3 | 97.1 | 96.9 | 96.2 | 95.4 | 94.6 | 93.9 | 93.1 | 92.3 |
| 11.2 | 97.6 | 97.4 | 97.3 | 97.2 | 97.0 | 96.3 | 95.5 | 94.7 | 94.0 | 93.2 | 92.4 |
| 11.4 | 97.7 | 97.5 | 97.4 | 97.2 | 97.1 | 96.3 | 95.6 | 94.9 | 94.1 | 93.4 | 92.6 |
| 11.6 | 97.7 | 97.5 | 97.4 | 97.3 | 97.1 | 96.4 | 95.7 | 95.0 | 94.2 | 93.5 | 92.8 |
| 11.8 | 97.7 | 97.6 | 97.5 | 97.3 | 97.2 | 96.5 | 95.8 | 95.1 | 94.4 | 93.6 | 92.9 |

b = % $SO_2$ in exit gas

$$x = 100\left((2a - 2b) \Big/ \left(2a - \frac{3ab}{100}\right)\right)$$

solution in a graduated cylinder and then diluting this with water to 1000 ml in a 1000-ml graduated cylinder.

Keep all iodine solutions in brown bottles in a cool place. Always replace the glass stoppers as soon as possible.

Starch solution sours quickly because of bacterial and mold growth, and then turns the iodine solution brown instead of blue so that a clear end point is not obtained. Prepare fresh starch solutions weekly, or more often in warm weather. A starch solution prepared as follows, however, will keep for months without deterioration or loss of sensitivity.

Dissolve 2 grams of powdered starch in 400 ml of cold distilled water. Dissolve 6 grams of caustic soda in a small amount of distilled water and add to the starch solution, stirring until dissolved. Let stand 1 hour for complete solution; the liquid should be uniformly translucent. Neutralize the alkali by adding concentrated hydrochloric acid (about 15 ml) until the solution is just acid to litmus paper. A slight excess of acid is beneficial in preserving the indicator.

**Reich Test for Sulfur Dioxide** (For sulfur-burning plants of air-quench type)

Entrance Gas Test — Flush the sample line thoroughly with gas before the test to insure getting a sample representative of operation at the time that the test is being made.

Fill the shaker bottle approximately two-thirds full of water and add about 5 ml of starch solution. Add 10 ml of N/10 iodine to the bottle by pipette, after first bringing the solution to a *faint* blue color by adding one or two drops of iodine solution. It is preferable to use the same water with starch indicator in the shaker bottle for a number of determinations. Either acidify new water in the shaker bottle with two drops of acid or repeat the first determination to obtain a good reading.

With all clamps and stopcocks, place the rubber stopper in the test bottle. Adjust the water level in the 250-cc burette to the "zero mark" by raising the water bottle with the glass stopcocks at the top and bottom of the burette open. Then close the top stopcock and place the water bottle back on the table. *Make sure that all connections in the apparatus are tight.*

Open the clamp on the sampling tube, adjusting it so that the gas bubbles pass *slowly* through the solution in the bottle. Shake the bottle continuously when gas is bubbling in to insure complete absorption of $SO_2$. Continue until the solution has changed to the same *faint* blue color obtained before. Be careful not to overrun the end point.

Close the clamp on the sampling line tightly when the end point has been reached. Raise the water bottle so that its water level is balanced against the water level in the burette, then note the amount of air that has been displaced in the burette. Note the temperature on the thermometer. Refer to Table B1 and to the column headed by the temperature nearest that noted during the test. Follow down this column to find the number nearest to the measured volume of air in the cylinder. Then read the corresponding percent $SO_2$ from the table. For example, if the temperature is 30°C and the measured volume is 145 ml then the strength of the gas is 8.0 percent.

Exit Gas Test — Leave the water aspirator that maintains suction on the exit gas sampling line running at all times to insure a representative sample of gas. If gas is flowing through the line, a slight suction will show on the manometer.

Now, in the exit gas apparatus, repeat the procedure used for the entrance gas test except use 10 ml of N/100 iodine solution instead of N/10 iodine solution. Note the volume of air displaced and the temperature as before, then refer to Table B2 for the percent $SO_2$.

Oxygen in Exit Gas — Make sure all rubber connections and stopcocks on the Orsat apparatus are tight. Adjust the level of the potassium pyrogallol solution so that the potassium pyrogallol just enters the small portion of the tube under the stopcock. Connect the Orsat to the exit gas sample line. Set the three-way cock to exhaust the atmosphere, then raise the leveling bottle until the water fills the sampling type. While the sample tube is still full of water, turn the three-way cock, open it to the gas sample line, then lower the leveling bottle and draw gas into the sample tube. Repeat this procedure about three times to be certain the sample is representative. The last sample must be measured very carefully. The sample line is under slight negative pressure; to be certain that the sample contains exactly 100 cc of gas, draw in about 110 cc and then turn the three-way cock to blank the sample line. Now raise the leveling bottle very slowly to the 100-cc mark and exhaust the excess gas to the atmosphere.

Turn the three-way cock so that the gas sample will flow into the tube filled with potassium pyrogallol solution By raising and lowering the leveling bottle you will force the gas through the solution, which will absorb the oxygen that was in the gas. (Be careful not to force any of the solution over into the sample tube.) After the gas sample has been bubbled through the potassium pyrogallol solution several times, adjust the solution to starting level and close the stopcock. Raise or lower the leveling bottle so that it is balanced against the water in the sample tube. The reading on the calibrated sample tube will be the percentage of $O_2$ that was in the sample, usually 6 to 12 percent.

*NOTE*: Allowance for $SO_2$ in the sample *is not necessary* because the $SO_2$ will be absorbed in the leveling bottle water. If mercury is used in the leveling bottle, then the percent $SO_2$ obtained in the exit gas test must be subtracted from the Orsat reading to get percent $O_2$.

Conversion Efficiency — Refer to Table B6 for the percentage conversion efficiency. For example, if the percentages in the exit gas are 8 percent $O_2$ and 0.20 percent $SO_2$, the conversion efficiency is 98.2 percent.

Solutions — The solution of N/100 iodine solution may be prepared with sufficient accuracy by measuring 100 ml of the standardized N/10 iodine solution in the graduated cylinder and then diluting this with water to 1000 ml in a 1000-ml graduated cylinder.

Keep all iodine solutions in brown bottles and in a cool place. Always replace the glass stoppers as soon as possible.

Starch solution sours quickly because of bacterial and mold growth, and then turns the iodine solution brown instead of blue so that a clear end point is not obtained. Prepare fresh starch solutions weekly, or even more often in warm weather. A starch solution prepared as follows, however, will keep for months without deterioration or loss of sensitivity.

Dissolve 2 grams of powdered starch in 400 ml of cold distilled water. Dissolve 6 grams of caustic soda in a small amount of distilled water and add to the starch solution, stirring until dissolved. Let stand 1 hour for complete solution; a uniform translucent liquid should be obtained. Neutralize the alkali by adding concentrated hydrochloric acid (about 15 ml) until the solution is just acid to litmus paper. A slight excess of acid is beneficial in preserving the indicator.

TABLE B6. $SO_2$ CONVERSION CHART FOR SULFUR-BURNING PLANTS WITH AIR QUENCH

| $O_2$ in exit gas, % | Percentage of $SO_2$ converted to $SO_3$ | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|
| | $SO_2$ in exit gases, % | | | | | | | | | |
| | 0.10 | 0.12 | 0.14 | 0.16 | 0.18 | 0.20 | 0.22 | 0.24 | 0.26 | 0.28 |
| 6.0 | 99.2 | 99.0 | 98.9 | 98.7 | 98.6 | 98.4 | 98.3 | 98.1 | 98.0 | 97.8 |
| 6.2 | 99.2 | 99.0 | 98.9 | 98.7 | 98.6 | 98.4 | 98.3 | 98.1 | 98.0 | 97.8 |
| 6.4 | 99.2 | 99.0 | 98.9 | 98.7 | 98.6 | 98.4 | 98.2 | 98.1 | 97.9 | 97.8 |
| 6.6 | 99.2 | 99.0 | 98.8 | 98.7 | 98.5 | 98.3 | 98.2 | 98.0 | 97.9 | 97.7 |
| 6.8 | 99.2 | 99.0 | 98.8 | 98.7 | 98.5 | 98.3 | 98.1 | 98.0 | 97.8 | 97.7 |
| 7.0 | 99.2 | 99.0 | 98.8 | 98.7 | 98.5 | 98.3 | 98.1 | 98.0 | 97.8 | 97.7 |
| 7.2 | 99.2 | 99.0 | 98.8 | 98.7 | 98.5 | 98.3 | 98.1 | 98.0 | 97.8 | 97.7 |
| 7.4 | 99.2 | 99.0 | 98.8 | 98.7 | 98.5 | 98.3 | 98.1 | 97.9 | 97.8 | 97.6 |
| 7.6 | 99.1 | 98.9 | 98.7 | 98.6 | 98.4 | 98.2 | 98.0 | 97.9 | 97.7 | 97.6 |
| 7.8 | 99.1 | 98.9 | 98.7 | 98.6 | 98.4 | 98.2 | 98.0 | 97.8 | 97.7 | 97.5 |
| 8.0 | 99.1 | 98.9 | 98.7 | 98.6 | 98.4 | 98.2 | 98.0 | 97.8 | 97.7 | 97.5 |
| 8.2 | 99.1 | 98.9 | 98.7 | 98.6 | 98.4 | 98.2 | 98.0 | 97.8 | 97.6 | 97.4 |
| 8.4 | 99.1 | 98.9 | 98.7 | 98.5 | 98.3 | 98.1 | 97.9 | 97.7 | 97.6 | 97.4 |
| 8.6 | 99.0 | 98.8 | 98.6 | 98.5 | 98.3 | 96.1 | 97.9 | 97.7 | 97.5 | 97.3 |
| 8.8 | 99.0 | 98.8 | 98.6 | 98.4 | 98.2 | 98.0 | 97.8 | 97.6 | 97.5 | 97.3 |
| 9.0 | 99.0 | 98.8 | 98.6 | 98.4 | 98.2 | 98.0 | 97.8 | 97.6 | 97.4 | 97.2 |
| 9.2 | 99.0 | 98.8 | 98.6 | 98.4 | 98.2 | 98.0 | 97.8 | 97.6 | 97.4 | 97.2 |
| 9.4 | 99.0 | 98.8 | 98.6 | 98.3 | 98.1 | 97.9 | 97.7 | 97.5 | 97.3 | 97.1 |
| 9.6 | 99.0 | 98.8 | 98.6 | 98.3 | 98.1 | 97.9 | 97.7 | 97.5 | 97.3 | 97.1 |
| 9.8 | 98.9 | 98.8 | 98.6 | 98.3 | 98.1 | 97.9 | 97.7 | 97.5 | 97.2 | 97.0 |
| 10.0 | 98.9 | 98.7 | 98.5 | 98.2 | 98.0 | 97.8 | 97.6 | 97.4 | 97.2 | 97.0 |
| 10.2 | 98.9 | 98.7 | 98.5 | 98.2 | 98.0 | 97.8 | 97.6 | 97.4 | 97.1 | 96.9 |
| 10.4 | 98.9 | 98.7 | 98.4 | 98.2 | 97.9 | 97.7 | 97.5 | 97.3 | 97.1 | 96.9 |
| 10.6 | 98.9 | 98.7 | 98.4 | 98.2 | 97.9 | 97.7 | 97.5 | 97.3 | 97.0 | 96.8 |
| 10.8 | 99.8 | 98.6 | 98.4 | 98.1 | 97.9 | 97.7 | 97.5 | 97.2 | 97.0 | 96.7 |
| 11.0 | 98.8 | 98.6 | 98.3 | 98.1 | 97.8 | 97.6 | 97.4 | 97.1 | 96.9 | 96.6 |
| 11.2 | 98.8 | 98.6 | 98.3 | 98.1 | 97.8 | 97.6 | 97.4 | 97.1 | 96.9 | 96.6 |
| 11.4 | 98.8 | 98.5 | 98.3 | 98.0 | 97.8 | 97.5 | 97.3 | 97.0 | 96.8 | 96.5 |
| 11.6 | 98.7 | 98.5 | 98.2 | 98.0 | 97.7 | 97.5 | 97.2 | 97.0 | 96.7 | 96.5 |
| 11.8 | 98.7 | 98.4 | 98.2 | 97.9 | 97.7 | 97.4 | 97.2 | 96.9 | 96.7 | 96.4 |
| 12.0 | 98.7 | 98.4 | 98.2 | 97.9 | 97.7 | 97.4 | 97.1 | 96.9 | 96.6 | 96.4 |
| 12.2 | 98.7 | 98.4 | 98.1 | 97.9 | 97.6 | 97.3 | 97.0 | 96.8 | 96.5 | 96.3 |
| 12.4 | 98.6 | 98.3 | 98.1 | 97.8 | 97.5 | 97.2 | 96.9 | 96.7 | 96.4 | 96.2 |
| 12.6 | 98.6 | 98.3 | 98.0 | 97.8 | 97.5 | 97.2 | 96.9 | 96.6 | 96.4 | 96.1 |
| 12.8 | 98.6 | 98.3 | 98.0 | 97.7 | 97.4 | 97.1 | 96.8 | 96.5 | 96.3 | 96.0 |
| 13.0 | 98.5 | 98.2 | 97.9 | 97.6 | 97.3 | 97.0 | 96.7 | 96.4 | 96.2 | 95.9 |

TABLE B6 (Continued)

| $O_2$ in exit gas, % | Percentage of $SO_2$ converted to $SO_3$ | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|
| | $SO_2$ in exit gases, % | | | | | | | | | |
| | 0.30 | 0.32 | 0.34 | 0.36 | 0.38 | 0.40 | .425 | 0.45 | .475 | 0.50 |
| 6.0 | 97.7 | 97.5 | 97.3 | 97.2 | 97.0 | 96.8 | 96.6 | 96.4 | 96.2 | 96.0 |
| 6.2 | 97.7 | 97.5 | 97.3 | 97.2 | 97.0 | 96.8 | 96.6 | 96.4 | 96.2 | 96.0 |
| 6.4 | 97.6 | 97.4 | 97.2 | 97.1 | 96.9 | 96.7 | 96.5 | 96.3 | 96.1 | 95.9 |
| 6.6 | 97.6 | 97.4 | 97.2 | 97.1 | 96.9 | 96.7 | 96.5 | 96.3 | 96.0 | 95.8 |
| 6.8 | 97.5 | 97.3 | 97.2 | 97.0 | 96.9 | 96.7 | 96.5 | 96.3 | 96.0 | 95.8 |
| 7.0 | 97.5 | 97.3 | 97.1 | 97.0 | 96.8 | 96.6 | 96.4 | 96.2 | 95.9 | 95.7 |
| 7.2 | 97.5 | 97.3 | 97.1 | 97.0 | 96.8 | 96.6 | 96.4 | 96.2 | 95.9 | 95.7 |
| 7.4 | 97.4 | 97.2 | 97.0 | 96.9 | 96.7 | 96.5 | 96.3 | 96.1 | 95.8 | 95.6 |
| 7.6 | 97.4 | 97.2 | 97.0 | 96.9 | 96.7 | 96.5 | 96.3 | 96.0 | 95.8 | 95.5 |
| 7.8 | 97.3 | 97.1 | 96.9 | 96.8 | 96.6 | 96.4 | 96.2 | 96.0 | 95.7 | 95.5 |
| 8.0 | 97.3 | 97.1 | 96.9 | 96.8 | 96.6 | 96.4 | 96.2 | 95.9 | 95.7 | 95.4 |
| 8.2 | 97.2 | 97.0 | 96.8 | 96.7 | 96.5 | 96.3 | 96.1 | 95.9 | 95.6 | 95.4 |
| 8.4 | 97.2 | 97.0 | 96.8 | 96.7 | 96.5 | 96.3 | 96.1 | 95.8 | 95.6 | 95.3 |
| 8.6 | 97.1 | 97.0 | 96.8 | 96.7 | 96.5 | 96.2 | 96.0 | 95.7 | 95.5 | 95.2 |
| 8.8 | 97.1 | 97.0 | 96.8 | 96.6 | 96.4 | 96.2 | 96.0 | 95.7 | 95.5 | 95.2 |
| 9.0 | 97.0 | 96.9 | 96.7 | 96.6 | 96.4 | 96.1 | 95.9 | 95.6 | 95.4 | 95.1 |
| 9.2 | 97.0 | 96.8 | 96.6 | 96.4 | 96.2 | 96.0 | 95.8 | 95.5 | 95.3 | 95.0 |
| 9.4 | 96.9 | 96.7 | 96.5 | 96.3 | 96.1 | 95.9 | 95.7 | 95.4 | 95.2 | 94.9 |
| 9.6 | 96.9 | 96.7 | 96.5 | 96.3 | 96.1 | 95.9 | 95.6 | 95.4 | 95.1 | 94.8 |
| 9.8 | 96.8 | 96.6 | 96.4 | 96.2 | 96.0 | 95.8 | 95.5 | 95.3 | 95.0 | 94.7 |
| 10.0 | 96.8 | 96.6 | 96.4 | 96.1 | 95.9 | 95.7 | 95.4 | 95.2 | 94.9 | 94.6 |
| 10.2 | 96.7 | 96.5 | 96.3 | 96.0 | 95.8 | 95.6 | 95.3 | 95.1 | 94.8 | 94.5 |
| 10.4 | 96.7 | 96.5 | 96.2 | 96.0 | 95.7 | 95.5 | 95.2 | 95.0 | 94.7 | 94.4 |
| 10.6 | 96.6 | 96.4 | 96.2 | 95.9 | 95.7 | 95.5 | 95.2 | 94.9 | 94.6 | 94.3 |
| 10.8 | 96.5 | 96.3 | 96.1 | 95.8 | 95.6 | 95.4 | 95.1 | 94.8 | 94.5 | 94.2 |
| 11.0 | 96.4 | 96.2 | 96.0 | 95.7 | 95.5 | 95.3 | 95.0 | 94.7 | 94.4 | 94.1 |
| 11.2 | 96.4 | 96.2 | 95.9 | 95.7 | 95.4 | 95.2 | 94.9 | 94.6 | 94.3 | 94.0 |
| 11.4 | 96.3 | 96.1 | 95.8 | 95.6 | 95.3 | 95.1 | 94.8 | 94.5 | 94.2 | 93.9 |
| 11.6 | 96.2 | 96.0 | 95.7 | 95.5 | 95.2 | 95.0 | 94.7 | 94.4 | 94.0 | 93.7 |
| 11.8 | 96.2 | 95.9 | 95.7 | 95.4 | 95.2 | 94.9 | 94.6 | 94.3 | 93.9 | 93.6 |
| 12.0 | 96.1 | 95.8 | 95.6 | 95.3 | 95.1 | 94.8 | 94.5 | 94.2 | 93.8 | 93.5 |
| 12.2 | 96.0 | 95.7 | 95.5 | 95.2 | 95.0 | 94.7 | 94.4 | 94.0 | 93.7 | 93.3 |
| 12.4 | 95.9 | 95.6 | 95.3 | 95.1 | 94.8 | 94.5 | 94.2 | 93.9 | 93.5 | 93.2 |
| 12.6 | 95.8 | 95.5 | 95.2 | 95.0 | 94.7 | 94.4 | 94.0 | 93.6 | 93.3 | 93.0 |
| 12.8 | 95.7 | 95.4 | 95.1 | 94.8 | 94.6 | 94.2 | 93.9 | 93.5 | 93.2 | 92.9 |
| 13.0 | 95.6 | 95.3 | 95.0 | 94.7 | 94.4 | 94.1 | 93.7 | 93.4 | 93.1 | 92.7 |

Methods for the preparation of 0.1 N iodine and starch solutions are as follows:

*Starch* — Boil a mixture of 1 gram of soluble starch and 50 ml water. Cool, add 0.5 gram potassium iodide, and dilute to 50 ml.

*0.1 N Iodine* — Dissolve 400 grams potassium iodide in about 2 liters of hot water. Add 218 grams iodine and heat to effect solution. Dilute to about 15,800 ml. Let stand 1 month before cutting. Adjust the normality to between 0.0095 and 0.1005 using 25-ml portions. Store in a dark place until needed. Keep two bottles prepared (not cut) in reserve.

Standardization — Standardize by withdrawing 45-ml portions from a burette into a 500-ml iodine flask containing 30 ml cold water. Add 1 ml concentrated HCl and let stand in an ice bath until fumes are absorbed. Titrate with 0.1 N sodium thiosulfate, swirling the contents of the flask continuously. When the solution becomes straw colored, add a few drops of fresh starch solution. Continue the titration until 0.02 ml of the sodium thiosulfate solution removes the blue color. Determine in triplicate.

Calculations — $\text{Log N } I_2 = \text{Log N Thio} + \text{Log ml Thio} - \text{Log ml } I_2$;

$$\text{or Normality } I_2 = \frac{(\text{ml Thio})\ (\text{N Thio})}{\text{ml } I_2}$$

## Determination of Moisture Content of Acid-Dried Air Gas in Contact Sulfuric Acid Plants

Choose a convenient sampling location on the pressure side of the blower unless you wish to determine moisture content between the drying tower and blower. A ¼-inch steel pipe with an all-iron gate valve closed to the flue may be used for the sample connection. Before making a test, clean the line thoroughly to remove any acid or acid sulfate that may have collected. Another suitable type of sampling connection may be made by welding a 1-inch pipe coupling to the flue and extending a glass sample tube through it. The sample tube may be held in place by means of a one-hole rubber stopper, (see Figure B5).

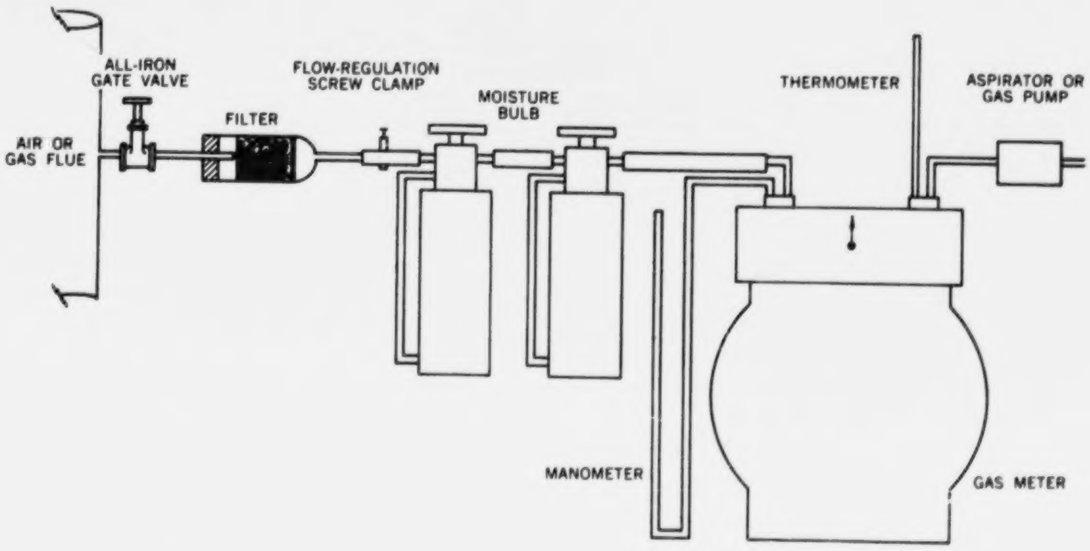


Figure B5 — Apparatus for determination of moisture content of acid-dried air or gas in contact sulfuric acid plants.

For removal of any acid particles or other foreign material from the sample, connect a filter to the sample line. Either of two types of filter may be used:

1. A Gooch-type filtering funnel (E. H. Sargent & Co., Cat. No. S-24485) packed with acid-washed, ignited, dry asbestos supported on a perforated porcelain plate in the bottom of the funnel. The asbestos should be packed tightly enough to function efficiently but not tightly enough to seriously restrict the gas flow. If the air or gas contains an appreciable amount of acid use two filters in series.
2. A Buchner-type, medium porosity, fritted-glass filter with a capacity of 30 ml (Cat. L.P. 21, page 146, Corning Glass Works, Corning, New York) may be used. The pressure drop through the glass filter may be too great to allow a sufficient flow of gas through the testing equipment without the use of a vacuum pump or aspirator.

Make the connection between the sample line and the filter with a minimum length of rubber tubing or preferably with no rubber at all.

Allow several cubic feet of gas to flow through the sample line and filter bulb so that the moisture in the system reaches equilibrium with the gas sample. The gas flow may be regulated by the valve in the sample line and also by a screw clamp in the line after the filter. After blowing out the line and filter, close the clamp at the end of the filter to keep the line and filter dry.

Connect to the filter two moisture absorption bulbs accurately weighed in grams to four decimal places. Nesbitt bulbs (E. H. Sargent & Co. Cat. S-22015) are recommended because they can be closed easily and are large enough in diameter to allow a relatively low gas velocity during the test. Large glass-stopper U tubes are also satisfactory. The bulbs may be packed by three methods:

1. Phosphorous pentoxide, the preferred absorbent, has the disadvantage of "gas channeling" unless packed properly. The following method is recommended. First place about ¾ inch of glass wool in the bottom of the Nesbitt bulbs. Then cut some glass wool into lengths ¼ inch or shorter and mix with $P_2O_5$ to coat the glass fiber. Pack this mixture in the bulbs, using first a ¾-inch layer of the $P_2O_5$ alone, and then alternating layers until the bulb is about three-quarters full. The final layer should be glass wool alone to prevent blowing $P_2O_5$ from the bulb. Close the stopcocks as soon as possible.
2. Pack the bulbs with a mixture of $P_2O_5$ and a carrier such as Drierite (anhydrous calcium sulfate). This mixture is easy to handle and does not "channel" easily.
3. Anhydrone (pure anhydrous magnesium perchlorate) may be used as an absorbent, but it is recommended that only the first bulb be packed with Anhydrone and the second with $P_2O_5$.

Tightly packed areas might obstruct the flow of gas and should be avoided. Resistance through each bulb should be less than 10 inches water gauge pressure when passing 5 cubic feet per hour. The gas is drawn down the side tube and up through the bulb. Fasten the stopcocks with thin copper wire to prevent blowing them out during the test. Use a minimum amount of stopcock grease to prevent grease getting into the gas inlet and outlet arms. If a loss in weight occurs in the second bulb, it is probably due to particles of the absorbing material or of the glass wool being blown out of the bulb, and the glass wool mat should be replaced.

If the moisture test is run on $SO_2$ gas rather than air, pass a few cubic feet of the gas to be sampled through the bulbs before they are weighed the first time after being packed.

The bulbs should be connected by a short piece of rubber tubing, which must fit snugly and be clean and free from cracks.

Connect a flowmeter to the second moisture bulb; also provide a thermometer for measuring the temperature and a manometer for measuring the static pressure of the gas passing through the meter. Use a gas meter (Sprague, Type 1A, Laboratory test meter, Cat. No. 16, p. 21, Sprague Meter Company, Bridgeport, Conn.) or a calibrated orifice flowmeter.

Very slightly open the flow-regulation screw clamp between the filter and bulbs, then open the stopcocks on the moisture bulbs. This procedure keeps the bulbs under slight pressure so that they cannot absorb moisture from the exit line to the flowmeter.

Allow the gas to flow through the apparatus at about 5 cubic feet per hour. The total sample should be 15 to 20 cubic feet. Record the meter reading, temperature, and pressure periodically. Unless a vacuum pump or aspirator is used, the meter pressure will be barometric pressure. Maintain a steady flow.

At the end of the test close the moisture bulbs and then the flow-regulation screw clamp.

Reweigh the moisture bulbs. When the bulbs are weighed before and after the test, they should be cleaned carefully and desiccated. At least 90 percent of the total increase in weight should occur in the first bulb. Use the bulb until it is evident that the first bulb is not absorbing as much as 90 percent of the moisture. Then use the second bulb as the number one bulb, and repack the first bulb for use as the second bulb. Weigh the bulbs immediately before and after the test.

Calculate the volume of sample as cubic feet at standard conditions.

Express the moisture as milligrams of water per cubic feet of dry gas at standard conditions.

For interpretation and comparison of test results, it is essential to report any pertinent operating data, including production rate and gas strength or the air or gas volume, with the test results.

### Determination of Acid Content of Acid-Dried Air or Gas in Contact Sulfuric Acid Plants

Extend a right-angle glass sample tube into the flue approximately one-third the distance across it. The end of the tube should face into the gas stream. The tube should be of such diameter that when sampling at the desired rate of 8 to 12 cubic feet per hour, the gas velocity entering the tube is the same as the gas velocity in the flue. The velocity in the flue may be calculated from the plant production rate and the gas strength or may be determined by means of a pitot tube. The sampling connection may be made by welding a 1-inch coupling into the flue. The sample tube may be held in place by means of a one-hole rubber stopper (see Figure B6).

For removal of the acid particles from the sample, connect a series of filters directly to the sample tube. Use either of two types of filters:

1. The preferred filter is the Buchner type, medium-porosity, fritted-glass filter with capacity of 30 to 40 ml (Cat. L.P. 21, page 146, Corning

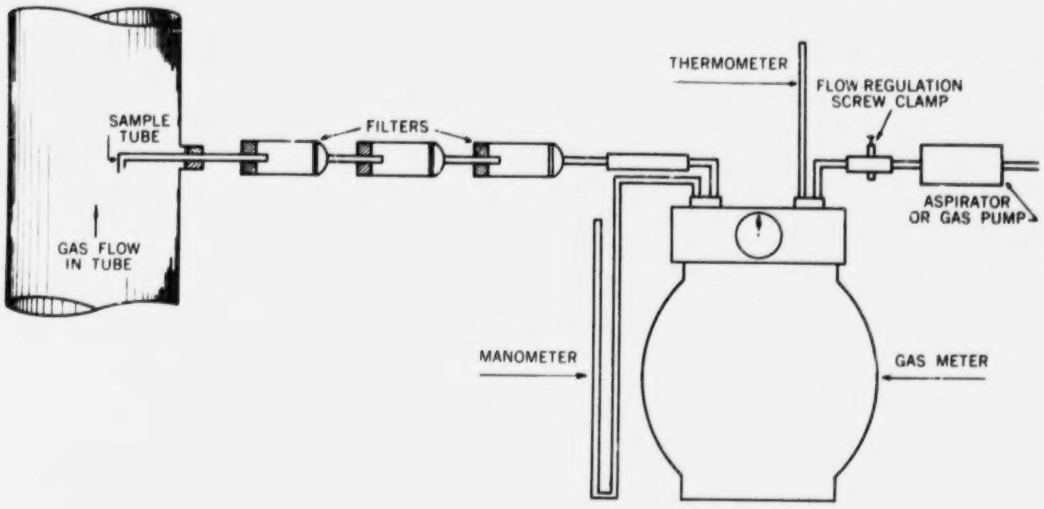


Figure B6 — Apparatus for determination of acid content of acid-dried air or gas and exit gas in contact sulfuric acid plants.

Glass Works, Corning, New York). Connect the filters by one-hole rubber stoppers. Use two filters in series for acid-dried air or gas and three filters in series for gas from the exit stack.

2. An alternative is a Gooch-type filtering funnel (E. H. Sargent & Co. Cat. No. S-24485) packed with acid-washed, ignited, dry asbestos supported on a perforated porcelain plate in the bottom of the funnel. Pack the asbestos tightly enough to function efficiently without seriously restricting gas flow. Use two or three filters in series for dry air or gas, and four filters for exit stack gas. The end of the sample tube and the end of the stem of each funnel should extend into the asbestos of the following funnel. Make a blank acidity determination on a portion of the asbestos before using it.

Glass filters are preferred because they are superior to asbestos filters for mist removal and are simpler to use. The pressure drop through glass filters is usually great enough to require the use of a vacuum pump or aspirator to draw sufficient flow of gas through the testing equipment.

Connect a flow meter to the end of the filter train; also provide a thermometer for measuring temperature and a manometer for measuring the static pressure of the gas passing through the meter. Use a gas meter (Sprague Type 1A Laboratory test meter, Cat. No. 16, page 21, Sprague Meter Company, Bridgeport, Conn.) or a calibrated orifice flow meter.

To draw the gas sample from the flue through the test apparatus, connect to the flow meter either a vacuum pump or an aspirator operated with air or water. A vacuum pump or aspirator is not required for tests on dry air or gas if the gas pressure is great enough to force the sample through the apparatus.

Regulate the gas flow by a screw clamp in the sampling line either before or after the filters, preferably after. If a vacuum pump or aspirator is used, the flow-regulation screw clamp should be after the flow meter instead of before or after the filters. If possible avoid the use of rubber connections in the sample line to the filters.

Allow the gas to flow through the apparatus at the calculated rate (8 to 10 cubic feet per hour). Record the meter reading, temperature, and pressure periodically. Maintain a steady flow.

Continue the test on dry air for about 5 to 6 hours, or if the gas is substantially acid-free, for 24 hours. Continue the test on exit gas for about 3 to 4 hours (25 to 40 cubic feet).

Disconnect the flow meter at the end of the test. Carefully remove the sample tube from the flue so that any acid that may have collected in the tube is not lost.

Wash the acid from the inside of the sample tube.

Wash the filters, with suction, until the washings are acid-free. Combine the washings with the sample tube solution. To check whether the filter bulbs caught all the acid in the sample, wash and titrate the last bulb.

If the gas tested contained $SO_2$, slowly boil the washings for 15 minutes to remove any dissolved $SO_2$.

Titrate the washings with standard NaOH (N/100 for dry air or gas, and N/20 for exit gas) to a methyl red end point. Express the acidity as milligrams of $H_2SO_4$.

Calculate the volume of the gas sample as cubic feet at standard conditions (0°C and 760 mm Hg).

Express the acid content of the gas as mg $H_2SO_4$ per cubic feet of dry gas at standard conditions.

For interpretation and comparison of test results, it is essential to report any pertinent operating data, including production rate and gas strength or the air or gas volume, with the test results.

### "Stick" Test for Determination of Sulfuric Acid Spray

To determine the quantity of mechanically entrained spray in the gas stream leaving the drying or absorbing towers, insert a clean, smooth, soft wood stick ¾ inch wide by ⅜ inch thick into the duct across the full diameter.

The test period will vary from 1 to 5 minutes, depending on the quantity of spray. Usually 1 minute of immersion is ample to indicate the presence of any appreciable quantity of spray. This test is by visual observation only and is only semi-quantitative.

A small amount of spray would consist of a few particles about the size of a pin head. A medium amount of spray would be indicated by additional spots and of about ⅛ inch diameter. Heavy spray would be shown in the droplets overlapped to present a wet surface with particle size approaching ¼-inch to ⅜-inch diameter.

This test is for true spray only and will not show mist unless the stick is immersed for several minutes; then mist will show up as an over-all blackening.

The term "mist" is intended to denote the extremely finely divided particles that escape from the mist precipitator or that enter an absorbing tower. The term "spray" is intended to mean those much larger droplets that may be mechanically entrained from drying or absorbing towers.

## SHELL DEVELOPMENT COMPANY METHOD FOR THE DETERMINATION OF SULFUR DIOXIDE AND SULFUR TRIOXIDE(*17*)

### Scope

This method describes a procedure for determining sulfur dioxide and sulfur trioxide in stack gases.

### Apparatus

*Sampling Probe* — Glass tubing (preferably borosilicate or quartz) of suitable size with a ball joint at one end and a removable filter at the other (a ½-inch-OD, 6-foot-long tube has been used). It may be necessary to support the glass probe in a stainless steel pipe; if the stack gas temperature exceeds 500°C, a water-cooled jacket of metal may be required.

*Filter* — A filter is needed to remove particulate matter, which may contain metal sulfates and cause interference during analysis. Borosilicate glass wool, Kaolin wool, or silica wool are suitable filters for removing particulate matter. (Ammonia or certain gaseous ammonia compounds have been reported to cause interference with sulfur trioxide determination(*21*).)

*Adapter* — Six plug-type connecting tubes T 24/40, one with a 90° bend and a socket joint.

*Heating Tape* — An insulated heating tape with a powerstat to prevent condensation in exposed portion of probe and adapter. Alternative: glass wool or other suitable insulators.

*Dry Gas Meter* — A 0.1-cubic-foot-per-revolution dry gas meter equipped with a fitting for a thermometer and a manometer. Alternately, a calibrated tank or a rotameter calibrated at the operating pressure may be used.

*Vacuum pump.*

*Thermometers* — One 10-50°C, ± 1°C; and one 0-300°C ± 5°C are suitable.

*Manometer* — A 36-inch-Hg manometer.

*Absorbers* — Two U-shaped ASTM D 1266 lamp sulfur absorbers with coarse-sintered plates.

*Filter Tube* — One 40-mm-diameter Corning medium-sintered plate.

*Scrubber for Purifying Air* — An ASTM D 1266 lamp sulfur absorber with coarse-sintered plate.

*Teflon Tubing* — Teflon tubing, ¼ inch ID, for connecting absorbers. Alternative: 8-mm pyrex tubing with butt-to-butt connections held together with Tygon.

(An alternate absorption system that will operate with less pressure drop has been used by a study group of the American Petroleum Institute(*23*). The absorption section consists of three absorbers and two spray traps as described in Section A-22 and 23 of the "Methods of Test for Sulfur in Petroleum Products and Liquified (LP) Gases (Lamp Method)," ASTM Designation D-1266-59T.)

### Reagents

*Water* — Distilled water that has been deionized.

*Isopropanol, Anhydrous.*

*80 Percent Isopropyl Alcohol* — Dilute isopropanol with water at a ratio of 4 to 1.

*30 Percent Hydrogen Peroxide* — (reagent grade).

*3 Percent Hydrogen Peroxide* — Dilute 30 percent hydrogen peroxide with water at a ratio of 10 to 1. Prepare fresh daily.

*Barium Chloride* — ($BaCl_2 \cdot 2\ H_2O$, reagent grade).

*0.0100N Alcoholic Barium Chloride* — Dissolve 1.2216 grams $BaCl_2 \cdot 2\ H_2O$ in 200 ml of water and dilute to 1 liter with isopropanol. Standardize this solution with 0.01 N alcoholic sulfuric acid solution.

(As an alternate titrating solution to 0.01N alcoholic barium chloride, the American Petroleum Institute Study Group uses 0.01N alcoholic barium perchlorate because they believe that it gives a sharper end point during titration.)

*Thorin Indicator* — 1-(0-arsonophenylazo)-2 naphthol-3, 6-disulfonic acid, disodium salt.

*0.2 Percent Thorin Indicator* — Dissolve 0.2 gram thorin indicator in 100 ml water. Store in polyethylene bottle.

**Sampling Procedure**

Set up the apparatus as shown in Figure B7. Place 30 ml of 80 percent isopropyl alcohol in the first absorber and 10 ml in the filter tube. Then add 50 ml of 3 percent hydrogen peroxide to the second absorber. A light film of silicone grease on the upper parts of the joints may be used to prevent leakage. Wind the heating tape in a uniform single layer around the exposed portion of the probe and adapter and cover the heating tape with asbestos tape wound in the opposite direction. Place a thermometer between the heating tape and asbestos as near the adapter joint as possible. Connect the heating tape to a powerstat, switch on the current, and maintain the probe and adapter at a temperature at which no condensation will occur (about 250°C). Sample at 0.075 cubic foot per minute until 2 cubic feet or a suitable volume of gas has been sampled. Record the meter readings, temperatures, and pressures at 10-minute intervals. Note the barometric pressure. Do not sample at a vacuum of more than 8 inches Hg.

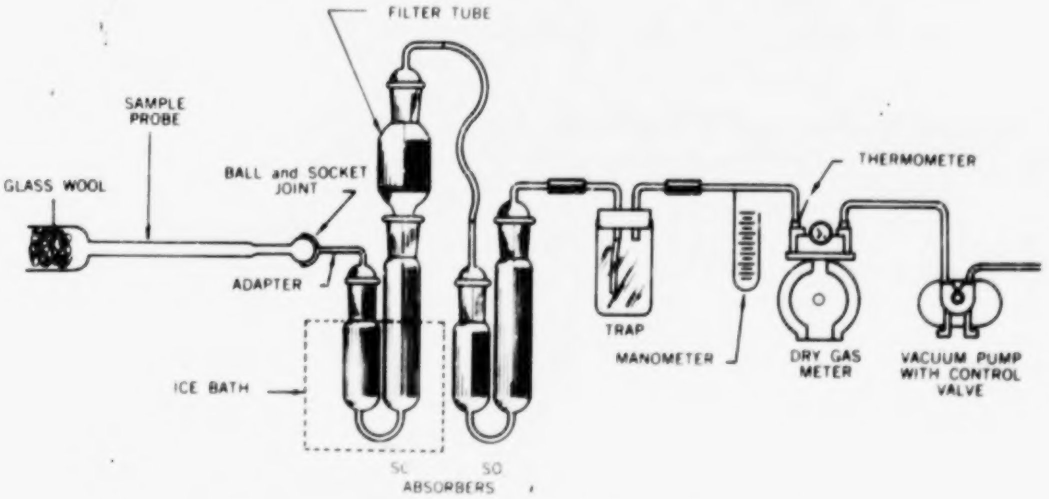


Figure B7 — Sulfur dioxide - sulfur trioxide sampling train.

### Sample Preparation

Disconnect the asbestos tape, heating tape, probe, and adapter and allow them to cool. Connect the scrubber for purifying air to the inlet of the isopropyl alcohol absorber and add 50 ml of 3 percent hydrogen peroxide. Replace the water in the ice bath with tap water. Draw air through the system for 15 minutes to transfer residual sulfur dioxide to the hydrogen peroxide absorber. Disconnect the purifying air scrubber. (Although the use of air for removal of sulfur dioxide from isopropyl alcohol should not result in oxidation of sulfur dioxide to sulfur trioxide, the American Petroleum Institute Joint Study Group uses 99 percent nitrogen to preclude any possibility of oxidation.) Remove the filter and wash the probe and adapter with 80 percent isopropyl alcohol. Place the washings in the isopropyl alcohol absorber.

Disconnect the hydrogen peroxide absorber and transfer the contents and the water washings to a 250-ml volumetric flask. Dilute with water to the mark. Analyze for sulfur dioxide.

Stopper the isopropyl alcohol absorber and apply suction to the filter end. Remove the suction line and allow the partial vacuum in the absorber to draw the solution from the filter. Rinse the filter tube with 80 percent isopropyl alcohol before the suction is lost. Transfer the contents of the isopropyl alcohol absorber and its washings to a 250-ml volumetric flask and dilute to the mark with 80 percent isopropyl alcohol. Analyze for sulfur trioxide.

### Analytical Procedure

Sulfur Trioxide — Pipet a suitable aliquot to a flask and dilute to 100 ml with 80 percent isopropyl alcohol. Add a few drops of thorin indicator (enough to give a yellow color). Titrate with 0.01N $BaCl_2$ to the pink end point. Make a blank determination in parallel.

Sulfur Dioxide — Transfer a suitable aliquot to a flask and add 4 times this volume of isopropyl alcohol. Dilute to 100 ml with 80 percent isopropyl alcohol, add enough thorin indicator to give a yellow color, and titrate with standard 0.01N $BaCl_2$ to the pink end point. Run a blank determination in parallel.

### Calculations

$$\text{ppm } SO_2 \text{ or } SO_3 \text{ by volume} = \frac{24(A-B)\ (N)\ (F)\ (T)}{(V_o)\ (P)}$$

| | | |
|---|---|---|
| where | $A$ | 0.01N $BaCl_2$ used for titration of sample |
| | $B$ | ml 0.01N $BaCl_2$ used for titration of blank |
| | $N$ | exact normality of $BaCl_2$ |
| | $F$ | dilution factor |
| | $T$ | average meter temperature, °R |
| | $V_o$ | observed volume of gas sample, cu ft |
| | $P$ | average absolute meter pressure, in. Hg |

## CHEMICAL CONSTRUCTION CORPORATION METHODS FOR GAS ANALYSIS AT CONTACT SULFURIC ACID PLANTS

### Reagents

*Hydrogen peroxide solution, 0.2N* — Dilute 20 ml of 30 percent hydrogen peroxide to 2 liters with distilled water in a volumetric flask. Add 0.4 gram of ascorbic acid (inhibitor) and store in a dark bottle. Standardize daily.

*0.1N — Potassium permanganate* — Dissolve 6.6 grams of potassium permanganate in about 2100 ml of distilled water in a large Erlenmeyer flask. Boil gently for 20 to 30 minutes. Stopper and allow to stand for several days in the dark.

Decant through an asbestos filter into a brown bottle. Do not wash the undissolved residue.

*0.05N — Sodium hydroxide solution*
*0.1N — Sodium hydroxide solution*
*Phenolphthalein indicator*
*Methyl red indicator*
*Dilute sulfuric acid (1:1)*
*Sodium hydroxide solution, 25 percent*

**Apparatus**

*Train* — for analyzing converter entrance gas (Figure B8)
*Portable apparatus* — for analyzing stack gas (Figure B9)
*Two 50-ml burettes.*
*Pipettes* — 25 and 50 ml
*Volumetric flasks* — 250 and 500 ml
*Gas scrubber* — 250-ml volume

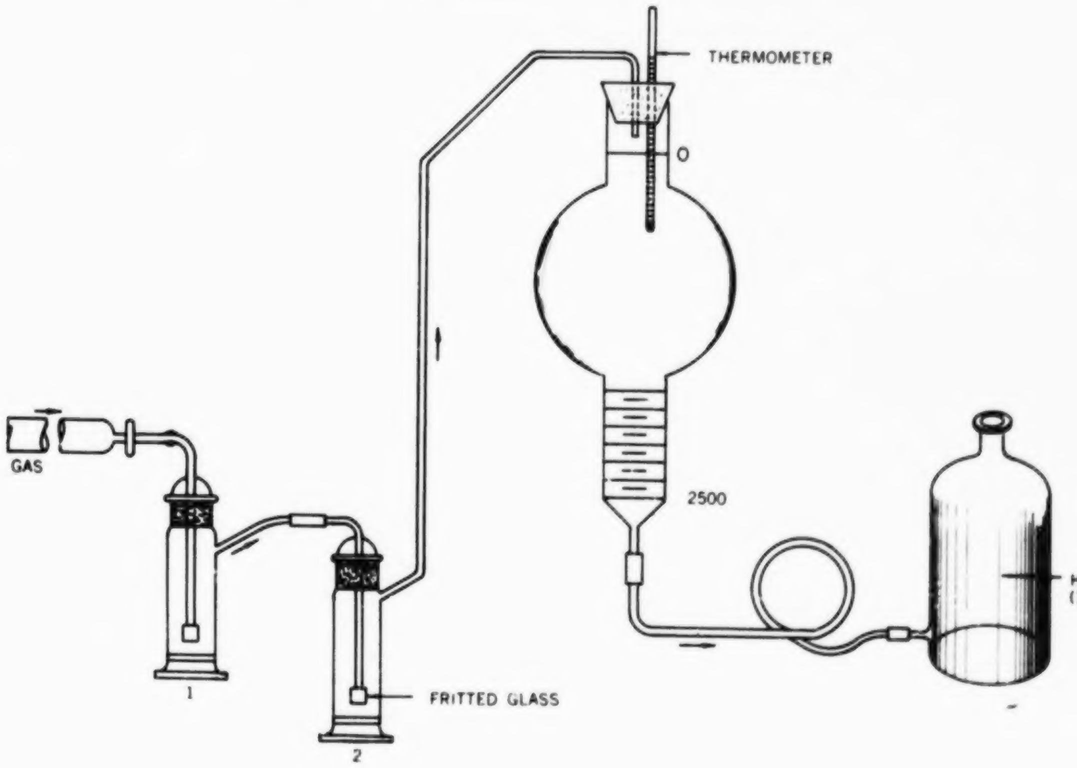


Figure B8 — Train for analysis of converter entrance gas.

*Sampling probe.* The diameter of the sampling tube is considered so that the gas is sampled isokinetically.

$V = fa$
$V$ = Volume flow rate of gas, cfm
$f$ = Linear flow of gas stream, lfm
$a$ = Area of stack, ft$^2$

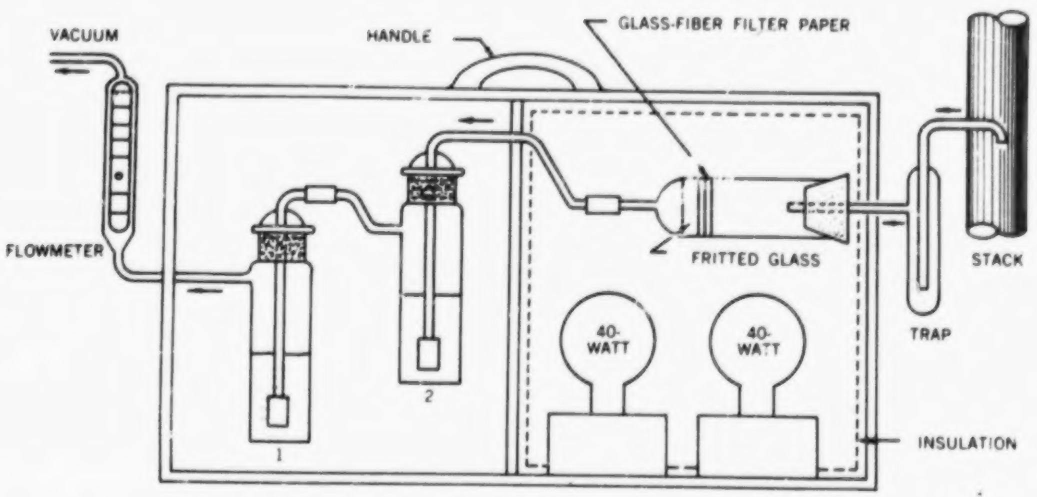


Figure B9 — Portable apparatus for determination of acid mist, $SO_2$, and $SO_3$.

**Standardization of Hydrogen Peroxide Solution**

Transfer 25.0 ml of the hydrogen peroxide solution to a 600-ml beaker containing about 250 ml of distilled water. (The same pipette is used for the standardization and the analysis.)

Add 10 ml of dilute sulfuric acid (1-1).

Titrate with 0.1N $KMnO_4$ until the pink color holds for 30 seconds after the addition of one drop.

The volume of 0.1N $KMnO_4$ required for 25.0 ml of hydrogen peroxide = A. This volume is called the blank and is usually 40 to 50 ml. The hydrogen peroxide solution is standardized daily. The addition of ascorbic acid helps to reduce decomposition of $H_2O_2$.

**Analysis of Converter Entrance Gas**

Gas sampling train (see Figure B8) consists of:

Kel-F tubing, ¼-inch bore, used for all connections.

Two gas washing bottles, 250-ml, with extra-coarse fritted glass.

Calibrated gas measuring flask made from a 2-liter round bottom flask and a 250-ml burette.

A 4-liter aspirator bottle containing about 3 liters of 10 percent sulfuric acid with methyl red indicator.

Rubber stopper and thermometer.

Place 75.0 ml of the O.2N — hydrogen peroxide solution in the first gas washing bottle and 50.0 ml in the second bottle.

Add 50 ml of distilled water to each bottle.

Fill measuring flask to mark with the 10 percent sulfuric acid using the leveling bottle.

Before taking sample, purge line well.

Hook up apparatus and sample slowly. Sampling 2500 ml of gas should take about 15 minutes.

Measure volume of gas sample taken with the leveling bottle. Record temperature.

Disconnect and transfer hydrogen peroxide solution to a 500-ml volumetric flask. Wash gas washing bottles well. Dilute to mark with distilled water.

Fill a 250-ml volumetric flask by carefully pouring the solution in the 500-ml volumetric flask.

Wash the contents of each flask into two 600-ml beakers.

Add 10 ml of dilute sulfuric acid (1-1) to one beaker and titrate with 0.1N. $KMnO_4$ until the pink color holds for 30 seconds after the addition of one drop. ml of 0.1N $KMnO_4$ = B.

Add a few drops of phenolphthalein indicator to the second beaker and titrate with 0.5N NaOH. ml of 0.5 NaOH = C.

**Calculations**

$V_0$ = measured volume of gas (ml), sulfur free at temperature T.
T = Temperature, °C.
P = Barometric pressure, in. Hg.
W = Vapor pressure of water at T, in. Hg.
V = Calculated volume of sulfur free gas at standard conditions (760 mm Hg and 0°C.).

Normality $KMnO_4$ x (5A — 2B) x 10.95 = Vol. of $SO_2$ (ml) at standard conditions = R.

Normality NaOH x 2C x 10.95 = Vol. (ml) of $SO_2 + SO_3$ as $SO_2$ at standard conditions = S.

$$\frac{R}{V + S} \times 100 = \text{percent } SO_2$$

$$\frac{S}{V + S} \times 100 = \text{percent total as } SO_2$$

$$1.25\ (\text{percent total as } SO_2 - \text{percent } SO_2) = \text{percent } SO_3$$

### Determination of Sulfuric Acid Mist, Sulfur Dioxide, and Sulfur Trioxide in Stack Gas

Gas sampling train (see Figure B9) is a portable apparatus and consists of the following:

Glass sampling probe; sample is taken isokinetically.

Glass trap.

Sealing tube, 25 mm diameter with coarse-fritted disk for holding glass filter paper.

Two 40-watt tungsten lamps for keeping temperature of the fritted-glas tube above the dew point of water.

Portable vacuum pump, made by the Jordan Pump Co., Atlanta, Ga., Model No. NW-222.

Two gas washing bottles, 250-ml with extra-coarse-fritted glass.

Flow meter, Brooks, Mite, Brooks Rotameter Co., calibrated 0.45 to 4.5 lpm of air at STP.

Glass-fiber filter paper, 2.4-cm diameter, No. X-934-AH made by the Hurlbut Paper Company.

Place two glass-fiber filter papers in the sealing tube against the fritted disk so that the fit is good.

Place 25.0 ml of the 0.2N — hydrogen peroxide solution in each of the two gas washing bottles; add about 100 ml of distilled water to each bottle.

Connect train and check flow-meter rate before connecting sampling tube from stack. Gas rate should be 0.7 to 1.0 liters per minute. Tungsten lamps should be burning.

Connect sampling tube and take a 10.0-minute sample. Disconnect sample line and continue sucking air through train for 30 seconds. Shut off pump.

Volume of sample = X (liters at S.C.)

Replace the two gas washing bottles with a scrubber containing about 100 ml of 25 percent sodium hydroxide.

Continue taking the gas sample; increase the flow rate to 4 liters per minute. Continue sampling for exactly 30 minutes.

Volume of gas sample at high flow rate = Y (liters at S.C.)

Total volume of gas sample for mist analysis = X + Y = Z.

While taking the sample for the mist analysis, transfer the hydrogen peroxide solution in the gas washing bottles to a 500-ml volumetric flask. Wash bottles well and dilute to mark with distilled water. Mix.

Fill a 250-ml volumetric flask by carefully pouring the solution from the 500-ml volumetric flask.

Wash the contents of each flask into two 600-ml beakers.

Add 10 ml of dilute sulfuric acid (1-1) to one beaker and titrate with 0.1N $KMnO_4$ until the pink color holds for 30 seconds after the addition of one drop.

ml of 0.1N $KMnO_4$ = B.

Add a few drops of phenolphthalein indicator to the second beaker and titrate with 0.1N NaOH.

ml of 0.1N NaOH = C.

After taking the additional 30-minute sample, disconnect sampling line and continue to suck air through train for 30 seconds. Shut off pump.

Remove the fritted-glass sealing tube with the two glass-fiber filter papers. Wash and filter the contents into a small suction flask. Titrate with 0.1N NaOH using phenolphthalein indicator.

ml of 0.1N NaOH = D.

**Calculations**

Normality $KMnO_4$ x (2A — 2B) x 10.95 = Vol. of $SO_2$ (ml) at S.C. = R.

Normality NaOH x 2C x 10.95 = Vol. (ml) of $SO_2 + SO_3$ as $SO_2$ at S.C. = S.

$$\frac{R}{X + S} \times 100 = \text{percent } SO_2.$$

$$\frac{S}{X + S} \times 100 = \text{percent total as } SO_2.$$

1.25 x (percent total as $SO_2$ — percent $SO_2$) = percent $SO_3$.

$$\frac{\text{Normality NaOH} \times D \times 49}{0.03533\ Z} = \text{Mg } H_2SO_4 \text{ mist per scf.}$$

A = ml of 0.1N $KMnO_4$ required for 25.0 ml of the hydrogen peroxide solution.

*NOTE*: Normally the Reich Test is used for control analysis. The preceding analytical methods are more accurate and are particularly useful for analyzing gases containing high concentrations of sulfur trioxide.

## PHENOLDISULFONIC ACID METHOD FOR TOTAL NITROGEN OXIDES

### Scope

When sulfur dioxide is present in the gas to be sampled and/or the concentration range of the oxides of nitrogen is 5 to several thousand ppm, this method is used. Accuracy near the lower limit is questionable. This test is unsuitable for atmospheric sampling.

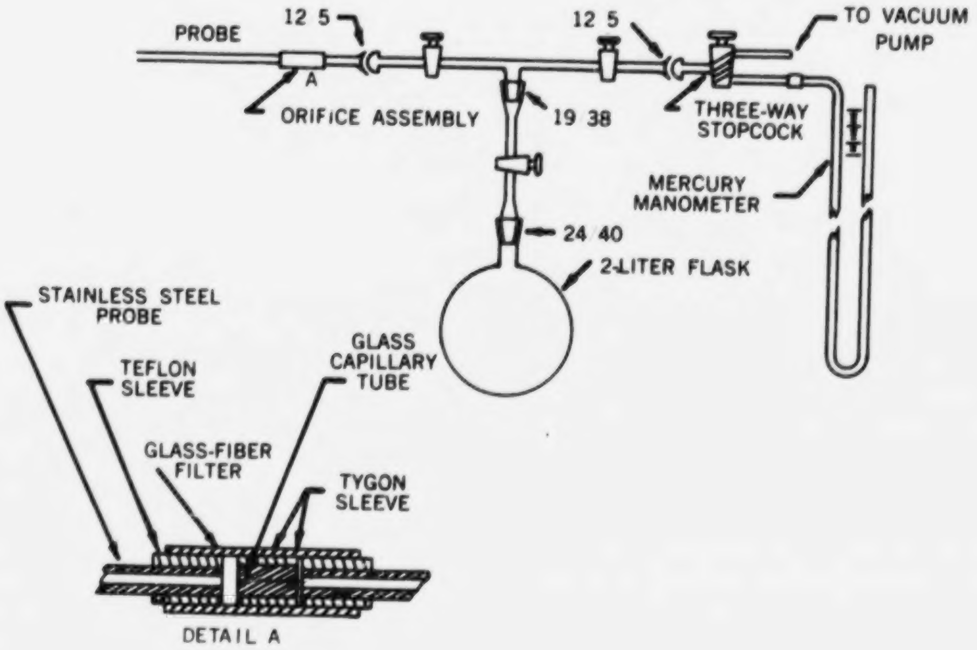

PROBE
12 5
12 5
TO VACUUM PUMP
A
ORIFICE ASSEMBLY
19/38
THREE-WAY STOPCOCK
MERCURY MANOMETER
24/40
2-LITER FLASK
STAINLESS STEEL PROBE
TEFLON SLEEVE
GLASS CAPILLARY TUBE
GLASS-FIBER FILTER
TYGON SLEEVE
DETAIL A

Figure B10 — Apparatus for integrated grab samples.

### Apparatus (Figure B10)

*Sampling Probe* — Stainless steel (type 304 or 316) or glass tubing of suitable size (¼-inch-OD, 6-foot-long stainless steel tubing has been used).

*Collection Flask* — A 2-liter round-bottom flask with an outer 24/40 joint for integrated samples or a 250-ml MSA sampling tube for grab samples.

*Orifice Assembly* — The size of the glass capillary tubing depends on the desired sampling period (flow rates of about 1 liter per minute have been used).

*Adapter with Stopcock* — Adapter for connecting collection flask to sampling T.

*Three-way Stopcock.*

*Manometer* — A 36-inch Hg manometer.

*Spectrophotometer* — Beckman Model B.

**Reagents**

*30 Percent Hydrogen Peroxide* — (reagent grade).

*3 Percent Hydrogen Peroxide* — Dilute 30 percent $H_2O_2$ with water at 1:1 ratio. Prepare fresh daily.

*Concentrated Sulfuric Acid.*

*0.1N (approximate) Sulfuric Acid* — Dilute 2.8 ml concentrated $H_2SO_4$ to 1 liter with water.

*Absorbing Solution* — Add 12 drops 3 percent $H_2O_2$ to each 100 ml 0.1N $H_2SO_4$. Make enough for required number of tests.

*In (approximate) Sodium Hydroxide* — Dissolve 40 gm NaOH pellets in water and dilute to 1 liter.

*Concentrated Ammonium Hydroxide.*

*Fuming Sulfuric Acid* — 15 to 18 percent weight free sulfuric anhydride (oleum).

*Phenol* (reagent grade).

*Phenoldisulfonic Acid Solution* — Dissolve 25 grams of pure white phenol in 150 ml concentrated $H_2SO_4$ on a steam bath. Cool and add 75 ml fuming sulfuric acid. Heat to 100°C for 2 hours. Store in a dark stoppered bottle. This solution should be colorless if prepared with quality reagents.

*Potassium Nitrate* (reagent grade).

*Standard Potassium Nitrate Solution* — Solution A: Dissolve 0.5495 gram $KNO_3$ and dilute to 1 liter in a volumetric flask. Solution B: Dilute 100 ml of Solution A to 1 liter. One ml of Solution A contains the equivalent of 0.250 mg $NO_2$ and of Solution B, 0.0250 mg $NO_2$.

**Calibration**

Calibration curves are made to cover different ranges of concentrations. Using a microburette for the first two lower ranges and a 50-ml burette for the next two higher ranges, transfer the following into separate 150-ml beakers (or 200-ml casseroles).

1. 0 — 100 ppm: 0.0 (blank), 2.0, 4.0, 6.0, 8.0, 10.0, 12.0, 16.0, 20.0 ml of $KNO_3$ Solution B.
2. 50 — 500 ppm: 0.0 (blank), 1.0, 1.5, 2.0, 3.0, 4.0, 6.0, 8.0, 10.0 ml of $KNO_3$ Solution A.

3. 500 — 1500 ppm: 0.0 (blank), 5.0, 10.0, 15.0, 20.0, 25.0, 30.0 ml of $KNO_3$ Solution A.

4. 1500 — 3000 ppm: 0.0 (blank), 15.0, 30.0, 35.0, 40.0, 45.0, 50.0, 55.0, 60.0 ml $KNO_3$ Solution A.

Add 25.0 ml absorbing solution to each beaker. Follow as directed in the Analytical Procedure section starting with the addition of 1N NaOH.

After the yellow color has developed, make dilutions for the following ranges as follows: 50 — 500 ppm (1:10), 500 — 1500 ppm (1:20) and 1500 — 3000 ppm (1:50). Read the absorbency of each solution at 420 $m\mu$.

Plot concentrations against absorbencies on rectangular graph paper. A new calibration curve should be made with each new batch of phenoldisulfonic acid solution or every few weeks.

### Sampling Procedure

Integrated Grab Sample — Add 25 ml freshly prepared absorbing solution into the flask. Record the exact volume of absorbing solution used.

Set up the apparatus as shown in Figure B10; attach the selected orifice. Purge the probe and orifice assembly with the gas to be tested before sampling begins by applying suction to it. Evacuate the system to the vapor pressure of the solution; this pressure is reached when the solution begins to boil. Record the pressure in the flask and the ambient temperature. Open the valve to the sampling probe to collect the sample. Constant flow will be maintained until the pressure reaches 0.53 of the atmospheric pressure. Stop before this point is reached. During sampling, check the rate of fall of the mercury in one leg of the manometer in case clogging, especially of the orifice, occurs. At the end of the sampling period, record the pressure, temperature, and barometric pressure.

An extended period of sampling can be obtained by following this procedure. Open the valve for only a few seconds at regular intervals. For example: Open the valve for 10 seconds and close it for 50 seconds; repeat every 60 seconds.

Grab Sample — Set up the apparatus as shown in Figure B11 for high concentrations (200-300 ppm) or the apparatus as shown in Figure B10 for low concentrations (0-200 ppm), but delete the orifice assembly. The same procedure is followed as in the method for integrated samples except that the valve is opened at the source for about 10 seconds and no orifice is used.

### Sample Preparation

Integrated Grab or Grab Sample — Shake the flask for 15 minutes and allow to stand overnight.

### Analytical Procedure

Transfer the contents of the collection flask to a beaker. Wash the flask three times with 15-ml portions of $H_2O$ and add the washings to the solution in the beaker. For a blank add 25 ml absorbing solution and 45 ml $H_2O$ to a beaker. Proceed as follows for the blank and samples.

Add 1N NaOH to the beaker until the solution is just alkaline to litmus paper. Evaporate the solution to dryness on a water bath and allow to cool. Carefully add 2 ml phenoldisulfonic acid solution to the dried residue and triturate thoroughly with a glass rod making sure that all the residue comes

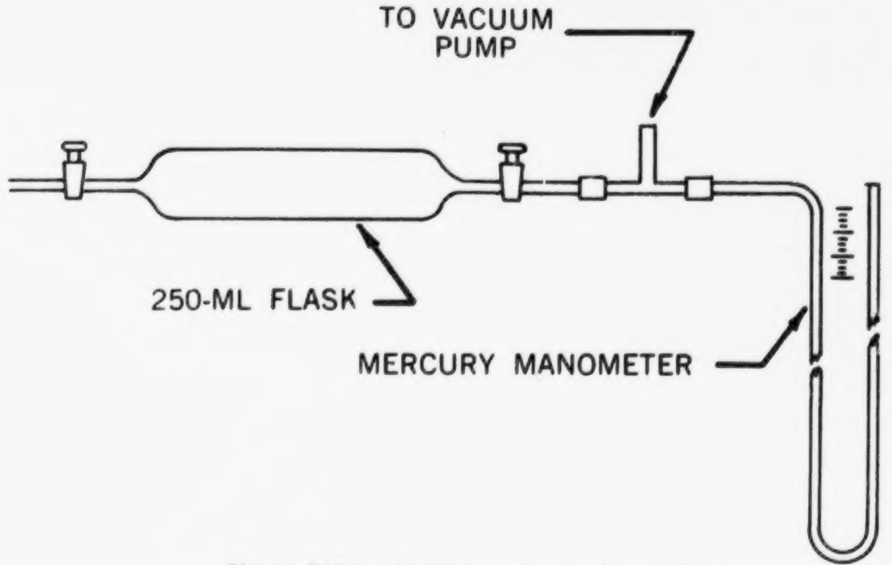


Figure B11 — Apparatus for grab samples.

into contact with the solution. Add 1 ml $H_2O$ and 4 drops concentrated $H_2SO_4$. Heat the solution on the water bath for 3 minutes with occasional stirring.

Allow the solution to cool and add 20 ml $H_2O$, mix well by stirring, and add 10 ml concentrated $NH_4OH$, dropwise, with constant stirring. Transfer the solution to 50-ml volumetric flask, washing the beaker three times with 4 to 5-ml portions of $H_2O$. Dilute to mark with water and mix thoroughly. Transfer a portion of the solution to a dry, clean centrifuge tube and centrifuge, or filter a portion of the solution.

Read the absorbency of each sample at 420 $m\mu$. If absorbency is higher than 0.6, make a suitable dilution of the sample and the blank and read the absorbency.

**Calculations**

$$\text{ppm } NO_2 = \frac{(5.24 \times 10^5)\ (C)}{V_s}$$

Where C = concentration of $NO_2$, mg (from calibration chart)

$V_s$ = gas sample volume at 70°F and 29.92 inches Hg, ml.

## SALTZMAN METHOD FOR NITROGEN DIOXIDE(*20*)

### Scope

A convenient but less accurate field method for determining $NO_2$ from stack gases utilizes the Saltzman reagent and glass syringes. Interference caused by air oxidation of NO to $NO_2$ and by $SO_2$ are minimized by expelling the gas sample immediately after the absorbing period and by reading the absorbence 15 minutes later.

### Apparatus

*Sampling Probe* — Stainless steel (type 304 or 316) or glass tubing of suitable size with two short taps close to one end and a filter at the other end.

*Serum Cap* — A self-sealing cap the size of the tap.

*Thermometer.*

*Collection Flask* — A 50- or 100-ml glass syringe.

*Gas Washing Bottle* — A 500-ml Erlenmeyer flask.

*Vacuum Pump.*

*Glass Wool.*

*Spectrophotometer* — Beckman Model B.

### Reagents

*Glacial Acetic Acid.*

*Sulfanilic Acid.*

*N-(1-naphthyl)-ethylenediamine Dihydrochloride*

*Absorbing Solution* — To 6 liters of water, add 1120 ml glacial acetic acid, 40 grams sulfanilic acid, and 0.160 grams N-(1-naphthyl)-ethylenediamine dihydrochloride. Dilute to 8 liters with water and store in a refrigerator; 45°F has proven adequate.

*Sodium Nitrite* (reagent grade).

*Standard Sodium Nitrite Solution* — Accurately weigh 2.03 grams $NaNO_2$ and dissolve in water. Dilute to 1 liter. Just before the standardization procedure, prepare a dilute standard sodium nitrite solution by transferring 10 ml of this stock solution to a 1-liter volumetric flask and diluting to 1 liter. One ml of this standard solution is equivalent to 10 $\mu$l of nitrogen dioxide at 25°C and 760 mm Hg.

*Sodium Hydroxide.*

*1N (approximate) Sodium Hydroxide* — Dissolve 40 grams NaOH and dilute to 1 liter with $H_2O$.

### Calibration

Transfer 0.2, 0.4, 0.6, 0.8, 1.0 and 1.2 ml of the standard sodium nitrite solution to six 25-ml volumetric flasks and fill the flask to the mark with the freshly prepared dilute absorbing solution. Shake thoroughly and allow 15 minutes for color development. Read the absorbence at 550 m$\mu$ in a spectrophotometer using the absorbing solution as the blank. The 1-ml standard is equivalent to 0.4 $\mu$l nitrogen dioxide per ml of reagent. Plot concentrations against absorbences on rectangular graph paper. Make a new calibration curve for each new batch of absorbing solution.

### Sampling Procedure

Set up the sampling train as shown in Figure B12. Place 200 ml 1N NaOH in the Erlenmeyer flask. Fill the syringe with a suitable volume of absorbing solution and cap the syringe. For a 100-ml syringe, 40 to 50 ml absorbing solution is adequate for a concentration range of 100-400 ppm.

Turn on the pump. After the probe is purged, uncap the syringe, insert the needle through the serum cap, and draw a sample to the 100-ml mark. Recap the syringe and shake vigorously for 1 minute. Expel the gas immediately thereafter. Record the temperature of the gas stream and the barometric pressure.

If $SO_2$ concentrations are 10 times greater than that of $NO_2$, add 1 ml acetone per 99 ml absorbing solution before its use.

### Analytical Procedure

After 15 minutes read the absorbence at 550 $m\mu$.

### Calculations

$$\text{ppm } NO_2 = \frac{V_r C\ (10^3)}{V_s}$$

Where $V_r$ = volume reagent, ml
$C$ = concentration of $NO_2$, $\mu$l/ml reagent
$V_s$ = volume of gas sample at 25°C and 760 mm Hg, ml

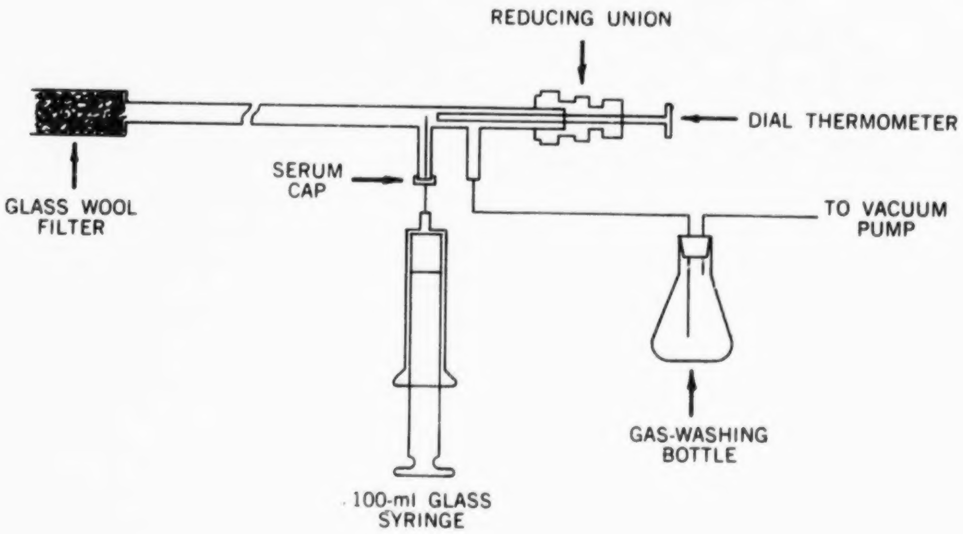

REDUCING UNION
DIAL THERMOMETER
SERUM CAP
GLASS WOOL FILTER
TO VACUUM PUMP
GAS-WASHING BOTTLE
100-ml GLASS SYRINGE

Figure B12 — Nitrogen dioxide sampling train.

# APPENDIX C: METHODS OF DETERMINING CAUSES OF VISIBLE PLUMES FROM STACKS OF CONTACT SULFURIC ACID PLANTS

Many factors, independently or in combinations, affect the visibility of stack emissions. Rarely will a single factor be the sole cause of visible plumes. Although much effort has been expended to provide easy methods for determining specific causes, correlating cause and effect is still an art rather than an exact procedure. The information assembled in this section is based on a history of experience in the operation of sulfuric acid plants. It is provided to aid operators in an orderly investigation to determine causes of stack-visibility problems.

**All Types of Units, Including Equipment from Drying Tower to Exit Stack**

| *CAUSE* | *METHOD OF DETERMINATION* |
|---|---|
| *Moisture in $SO_2$ gas or air* | |
| Poor drying. | Make moisture tests of air or gas leaving the drying tower. |
| Moist air leakage. | When the blower is located after the drying tower, make moisture test on air or gas in the blower discharge duct. (Atmospheric moisture may be drawn in the suction duct or connections of the blower.) |
| Poor acid distribution. Dirty distributor pan or tubes. Distribution points too far apart or acid not equally distributed in the area. Pan not level. | Inspect visually with and without acid circulating. Distributing points not more than 18-inch centers, no more than 12 inches from the inside of shell lining. |
| Insufficient acid circulating in the towers. | Measure acid level in pans with a rod. Make sure pans are level. Check amperage of pump motors. Compare temperature of gas or air leaving the drying tower with temperature of the acid entering the tower. They should be approximately the same. Check the increase in acid temperature across tower. |
| Channelling due to dirty tower. | Determine pressure drop through the tower, both including and excluding the spray catcher. Inspect visually for sulfate on the top of tower packing. Wash tower if necessary. |
| *Spray from drying tower* | Make stick test at exit duct. Two sticks at right angles to each other, and across the duct diameter, are necessary at times if flow pattern of gas including mist is distorted. |
| Splashing at weirs if the distributor is the weir type. | Examine visually with and without acid flowing. None of the weir streams should have any free drop from the bottom of the slots to the packing. Packing must come up to the bottom of each slot and should not splash at any weir. |
| Splash from leaking distributor tubes or leakage in the pans. | Examine visually with acid circulation both on and off. Look for wet tubes. |
| Splash from pans overflowing. | Measure each pan level with a rod. Instrument readings may be in error. Pans may not be level. |
| Leakage of internal acid piping. | Examine visually for leaks in internal acid pipe while acid is circulating at full normal rate. |

| *CAUSE* | *METHOD OF DETERMINATION* |
|---|---|
| Failure or plugging of entrainment separators. | Inspect. Measure pressure drop. Wash or repack spray catcher if necessary. |
| Spray from top surface of acid in distributor pan. | Inspect visually. Spray from distributor pan may result from improper entrance of acid from delivery pipe to pan. Air tapped in acid at pump may cause spray when released in the distributor pan. |
| Flooding of packing in the tower or flooding of packing at the acid distributor due to improper packing, high acid or gas flow, or breakdown of packing. | Flooding evidenced by high pressure differential. Visual inspection of tower internals will show uneven distribution of packing or "washing" effect causing packing to move and relocate in an uneven manner. |
| *Mist formed in system between converter outlet and absorbing tower.* | |
| Cooling in $SO_3$ cooler or economizer is too great, too fast, or localized. | Appearance of drip acid in the economizer or a larger-than-normal amount of drip acid drained from the $SO_3$ cooler shell. This condition may be aggravated by an abnormally high mist content in the $SO_3$ gas. |
| Duct cooling. | Note whether the poor appearance of the stack varies with atmospheric conditions. If appearance is worse during rainstorms, or during sudden changes in temperature and wind velocity, top shielding from rain or side shielding from wind may be required. |
| When large amounts of moisture are in the $SO_3$ gas leaving the converter, as from poor drying, entrained drying acid, inadequate gas purification, acidity or organic matter in the sulfur, etc., it is impossible to prevent acid mist formation. Much of the mist so formed cannot be removed in the absorbing tower and escapes as visible mist from the exit stack. | Can be detected quantitatively by mist tests of the gas entering and leaving the absorbing tower. Tyndall beam tests can be made on the gas leaving the equipment being tested. Sight glasses directly across the diameter of the absorbing tower, above the packing are helpful in determining whether the escape of fumes from the absorbing tower stack is due to unabsorbed $SO_3$ or sulfuric acid mist. The presence of mist in the gas will cause a cloudy appearance inside the tower. If the gas is clear inside the tower and the stack is fuming, the poor appearance of the stack is due to poor $SO_3$ absorption and not to mist in the gas. |
| *Absorbing tower operating conditions.* | |
| Temperature of acid in the tower may be too high or too low. | Low acid temperature has more effect on stack than high temperature. Usually the minimum is 50°C (122°F) and the maximum is 90°C (194°F) for acid entering. |

| *CAUSE* | *METHOD OF DETERMINATION* |
|---|---|
| | The optimum temperature must be found by operating experience. Lower temperatures are generally permitted with better quality gas that contains less $H_2SO_4$ mist or vapor. If stack appearance is poor due to mist or moisture condition, it can usually be improved by increasing the temperature of the acid going to the tower to 90° to 110°C. This is done only as a *temporary measure* to confirm that a mist or moisture condition exists. |
| Acid strength too high or too low. | Determine optimum strength by actual operation, adjusting slowly within the range of 98.5 percent to 99.4 percent. Approximately 99.2 percent is good practice. |
| Air leak at base of stack. | Visual inspection. |
| Temperature of gas entering tower. | In plants that do not produce oleum, temperatures of 150° to 160°C entering the absorber are low enough. Temperatures could be considerably higher with good stack appearance, but with higher gas inlet temperature the absorbing acid temperature must be higher also and corrosion will be greater. |
| Insufficient acid flow. | Measure acid level in pans with a rod. Make sure pans are level. Check amperage of pump motors. Compare temperature of gas or air leaving the drying tower with the temperature of the acid entering the tower. They should be approximately the same. Check the increase in acid temperature across tower. |
| Poor acid distribution. Dirty distributor pan. Distribution points too far apart or the acid not equally distributed in the area. | Inspect visually with and without acid circulating. Distributing points not more than 18-inch centers, nor more than 12 inches from the inside of shell lining. |
| Channelling due to dirty tower. | Determine pressure drop through the tower, both including and excluding the spray catcher. Inspect visually for sulfate on the top of tower packing. Wash tower if necessary. |
| Tower packing settled or disarranged. | When all other points have been checked and found satisfactory, this item might be the cause. Packing under the distributor tubes may have to be removed and rearranged. |

| *CAUSE* | *METHOD OF DETERMINATION* |
|---|---|
| *Oleum tower operating conditions.* | |
| Leakage of damper in $SO_3$ gas line bypassing the oleum tower, allowing subsequent mixture of hot and cooled gas streams. | Whenever possible avoid using a bypass line. When a bypass line cannot be avoided, try blanking it off to determine whether it affects the stack appearance. Damper leakage may be detected by measuring skin temperature of the bypass duct. If part of gas must pass through the oleum tower and part through the bypass, the temperature of the mixture going to the absorber should be above approximately 150° to 160°C; such a temperature usually results in a better stack. |
| **Sulfur Burning (Raw Gas) Units** | |
| *Steam or water leaks.* | |
| Sulfur line to burner. | Disconnect line at burner with pump down and steam on jacket. Blanking at pump may be necessary. At times it may be possible to cut steam off the steam jackets — carefully; stack will clear rapidly if a steam leak is the source of trouble. *Do not allow* sulfur in line to freeze. |
| Leaks in the boiler, superheater, or economizer tube. | Symptoms are a considerable increase in the condensed acid drip in $SO_3$ cooler and in the economizer or decrease in the amount of water required for dilution. When boiler leaks are suspected, shut down and examine by inspection for water dropping from boilers into the compartments or ducts under the boiler or economizer. If leaks are very large, water will run out of drain nozzles under the boiler or economizer when blind flange is removed from the end of the drains. Apply hydrostatic tests on boiler system equipment when leaks are suspected and cannot be detected. Comparative Tyndall beam tests can be made on gas entering and leaving equipment suspected of leaks. |
| *Oxides of nitrogen in gas.* | |
| Very high burner temperature causes nitrogen to combine with oxygen and form oxides of nitrogen, which tend to form sulfuric acid mist in the equipment between the converter and the absorbing tower. | Examine condensed drip in economizer or $SO_3$ cooler for niter. When drip is diluted with water, brown fumes will be noted if a considerable amount of niter is present. Niter in the burner gas may be prevented by reducing the burner temperature, lowering $SO_2$ gas strength, or lessening preheating of the air. This condition may be due to high localized temperatures that are |

| *CAUSE* | *METHOD OF DETERMINATION* |
|---|---|
| | not recorded or evident; it might be corrected by improving the sulfur spray distribution and burning pattern. |
| *Quality of the sulfur or raw material.* | Laboratory analysis of the raw material is required. |
| Nitrogen compounds. | May occur in any of the raw materials, i.e., sulfur, $H_2S$, or dilution acid (if unit uses spent acid in the tower acid circulating systems). |
| Hydrocarbon or organics in sulfur. | Good sulfur filtering sometimes helps by partially reducing organics. |
| Acidity in sulfur. | Neutralize acidity with lime, but only when sulfur is subsequently filtered. |
| **Metallurgical (Gas Purification) Units** | |
| *Mist.* | |
| Inefficient mist precipitators or coke filters. | Gas leaving the electrostatic precipitators (or leaving the coke filters) should be optically clear. Examine by Tyndall beam in gas duct leaving the precipitator or the coke box, or examine through sight glasses across the drying tower above the packing. Gas should be clear, not cloudy. |
| *Niter in the gas.* | |
| Arcing in the electrostatic precipitators forms ozone and oxides of nitrogen. | Arcing is visible through sight glasses in the precipitator, or audible from the crackling sparking, or will be noted from fluctuating volt meters. Sparking may be caused by broken wires, dirty wires, or swaying wires. Dirty wires usually are cleaned by washing, and then kept clean by flushing at timed intervals. |
| Niter from raw material, HCN in $H_2S$ gas, cyanide in the roasted ore, niter in $SO_2$ gas scrubbing or drying acids if partly mixed with chamber acid. | Laboratory analyses required. |

| | |
|---|---|
| B | Byproduct $SO_2$ gas from various sources |
| C | Copper converter gas |
| H | $H_2S$ |
| P | Pyrites or pyrrhotite |
| R | Spent or sludge acid |
| S | Frasch-process or recovered elemental sulfur, solid or liquid |
| Sc | Crude sulfur containing 15-25 percent S |
| Z | Zinc sulfide concentrates |

# APPENDIX D: SULFURIC ACID ESTABLISHMENTS IN THE UNITED STATES

The main purpose of this tabulation of sulfuric acid manufacturing establishments (Table D1) is to indicate the wide distribution and the principal areas of concentration of this industry throughout the country.

Information was drawn from various sources and is believed to represent the operable installations existing as of November 1, 1963, but not necessarily operating at that time. Listings are without regard to the number of producing units at a given location; the total number of units far exceeds the number of establishments. As a result of sale, merger, or lease, company identifications may in some cases differ from those presently in use, but should serve the intended purpose of general identification.

The contact process is shown at 163 establishments and the chamber process at 60 establishments, a total of 223 appearing in the list. Variance of these numbers from data given elsewhere in this report is not due to oversight or error, but to the use of a different basis of reporting.

Sources of sulfur dioxide in the raw materials column of Table D1 are keyed to the following abbreviations:

| | |
|---|---|
| B | Byproduct $SO_2$ from various sources. |
| C | Copper converter gas. |
| H | $H_2S$. |
| P | Pyrites or pyrrhotite. |
| R | Spent or sludge acid. |
| S | Frasch-process or recovered elemental sulfur, solid or liquid. |
| Sc | Crude sulfur containing 15 to 25 percent S. |
| Z | Zinc sulfide concentrates. |

## TABLE D1. SULFURIC ACID ESTABLISHMENTS IN THE UNITED STATES (As of November 1, 1963)

| Company | Location | Raw materials | Process |
|---|---|---|---|
| *ALABAMA* | | | |
| The American Agricultural Chemical Co. | Montgomery | S | Chamber |
| American Cyanamid Company | Mobile | S | Contact |
| E. I. du Pont de Nemours && Co. | Mineral Springs | S | Contact |
| Home Guano Company | Dothan | S | Chamber |
| Reichhold Chemicals, Incorporated | Tuscaloosa | S | Contact |
| Stauffer Chemical Company | Le Moyne | S | Contact |
| Tennessee Corporation, Lessee of Alabama Ordnance Works | Childersburg | S | Contact |
| V-C Chemical Co. — Division of Socony Mobil Oil Company | Dothan | S | Chamber |
| V-C Chemical Co. — Division of Socony Mobil Oil Company | Birmingh'm (Wylam) | S | Contact |
| *ARIZONA* | | | |
| Apache Powder Company | Benson | S | Contact |
| Bagdad Copper Company | Bagdad | S | Contact |
| Inspiration Consolidated Copper Co. | Inspiration | S | Contact |
| Kennecott Copper Corporation | Hayden | P | Contact |
| Southwest Agrochemical Corporation | Chandler | S | Contact |
| *ARKANSAS* | | | |
| Monsanto Company | El Dorado | S | Contact |
| Olin Mathieson Chemical Corporation | N. Little Rock | S | Contact |
| *CALIFORNIA* | | | |
| Allied Chemical Corporation, General Chemical Division | El Segundo | HRS | Contact |
| Allied Chemical Corporation, General Chemical Division | Bay Point | RS | Contact |
| Allied Chemical Corporation, General Chemical Division | Richmond | HRS | Contact |
| American Smelting & Refining Co. | Selby | B | Contact |
| Collier Carbon and Chemical Corp. | Wilmington | HRS | Contact |
| Monsanto Company | Avon | HRS | Contact |
| Occidental Petroleum Corporation, Best Fertilizer Co. Division | Lathrop | S | Contact |
| Stauffer Chemical Company | Dominguez | HRS | Contact |
| Stauffer Chemical Company | Vernon | S | Contact |
| Stauffer Chemical Company | Stege | S | Contact |
| Valley Nitrogen Producers, Inc. | Fresno | S | Contact |
| *COLORADO* | | | |
| Allied Chemical Corporation, General Chemical Division | Denver | PR | Contact |
| Rico Argentine Mining Co. | Rico | P | Contact |
| Union Carbide Corporation, Nuclear Div. | Uravan | S | Contact |
| *DELAWARE* | | | |
| Allied Chemical Corporation, General Chemical Division | Claymont | PR | Contact |

| Company | Location | Raw materials | Process |
|---|---|---|---|
| *FLORIDA* | | | |
| Acid Inc. | Mulberry | S | Contact |
| The American Agricultural Chemical Co. | Pensacola | S | Chamber |
| The American Agricultural Chemical Co. | Pierce | S | Chamber |
| American Cyanamid Company | Brewster | S | Contact |
| Armour and Company | Jacksonville | S | Chamber |
| Armour and Company | Bartow | S | Contact |
| Armour and Company | Fort Meade | S | Contact |
| W. R. Grace & Co., Davison Chemical Division | Ridgewood (Bartow) | S | Contact |
| International Minerals & Chemical Corp. | Mulberry (Bonnie) | S | Contact |
| F. S. Royster Guano Company | Pierce | S | Contact |
| Swift & Company | Agricola | S | Contact |
| U. S. Phosphoric Products Division, Tennessee Corporation | E. Tampa | S | Contact |
| V-C Chemical Co. — Division of Socony Mobil Oil Company | Nichols | S | Contact |
| Wilson & Toomer Fertilizer Co. | Jacksonville | S | Chamber |
| Wilson & Toomer Fertilizer Co. | Cottondale | S | Chamber |
| *GEORGIA* | | | |
| The American Agricultural Chemical Co. | Savannah | S | Chamber |
| American Cyanamid Company | Savannah | S | Contact |
| Armour and Company | Albany | S | Chamber |
| Armour and Company | Columbus | S | Chamber |
| Cotton States Fertilizer Co. | Macon | S | Chamber |
| Georgia Fertilizer Co. | Valdosta | S | Chamber |
| Minerals & Chemicals Phillip Corp. (Attapulgus Clay Products) | Attapulgus | B | Contact |
| Pelham Phosphate Co. | Pelham | S | Chamber |
| F. S. Royster Guano Company | Athens | S | Chamber |
| C. O. Smith Guano Co. | Moultrie | S | Chamber |
| Southern Fertilizers & Chemical Co. | Savannah | S | Contact |
| Southern States Phosphate & Fertilizer Company | Savannah | S | Chamber |
| V-C Chemical Co. — Division of Socony Mobil Oil Company | Savannah | S | Chamber |
| V-C Chemical Co. — Division of Socony Mobil Oil Company | Rome | S | Chamber |
| *HAWAII* | | | |
| Pacific Chemical & Fertilizer Co. (Pacific Guano Co.) | Honolulu | S | Contact |
| Standard Oil Co. of California, Western Operations, Inc. | Barbers Pt., Oahu | HRS | Contact |
| *IDAHO* | | | |
| The Bunker Hill Company (Sullivan Mining Company) | Kellogg | SZ | Contact |
| J. R. Simplot Company, Minerals & Chemical Division | Pocatello | S | Contact |

| Company | Location | Raw materials | Process |
|---|---|---|---|
| *ILLINOIS* | | | |
| Allied Chemical Corporation, General Chemical Division | Hegewisch | RS | Contact |
| Allied Chemical Corporation, General Chemical Division | E. St. Louis | RS | Contact |
| The American Agricultural Chemical Co. | E. Clinton | S | Chamber |
| American Cyanamid Company | Joliet | S | Contact |
| American Zinc Co. of Illinois | Fairmount City | SZ | Contact |
| American Zinc Co. of Illinois | Fairmount City | Z | Chamber |
| Armour and Company | Chicago Heights | S | Chamber |
| Hooker Chemical Corporation (National Phosphate Corporation) | Marseilles | S | Contact |
| Kankakee Ordnance Works | Joliet | S | Contact |
| Matthiessen & Hegeler Zinc Co. | La Salle | SZ | Chamber |
| Monsanto Company | Monsanto | S | Contact |
| National Distillers and Chemical Corp., U. S. Industrials Chemicals Co. Div. | Tuscola | S | Contact |
| Olin Mathieson Chemical Corporation, Blockson Chemical Division | Joliet | S | Contact |
| Chas. Pfizer & Co., Inc., C. K. Williams & Co. Division | E. St. Louis | B | Contact |
| Smith Douglass Co., Inc. | Streator | S | Contact |
| Swift & Company | Calumet City | S | Contact |
| *INDIANA* | | | |
| E. I. du Pont de Nemours & Co. | E. Chicago | RSZ | Contact |
| Marion Mfg. Co. | Indianapolis | S | Contact |
| Stauffer Chemical Company | Hammond | RS | Contact |
| *IOWA* | | | |
| The American Agricultural Chemical Co. | Humboldt | S | Chamber |
| International Minerals & Chemical Corp. | Mason City | S | Contact |
| National Distillers and Chemical Corp., U. S. Industrial Chemicals Co., Div. | Dubuque | S | Contact |
| *KANSAS* | | | |
| The Eagle-Picher Company | Galena | SZ | Contact |
| National Distillers and Chemical Corp., U. S. Industrial Chemicals Co., Div. | Sunflower (DeSoto) | RS | Contact |
| *KENTUCKY* | | | |
| E. I. du Pont de Nemours & Co. | Wurtland | RS | Contact |
| Pennsalt Chemicals Corporation | Calvert City | S | Contact |
| *LOUISIANA* | | | |
| Allied Chemical Corporation, General Chemical Division | Baton Rouge | RS | Contact |
| American Cyanamid Company | Avondale | S | Contact |
| Armour and Company | New Orleans | S | Chamber |
| Cities Service Company | Lake Charles | HRS | Contact |
| Olin Mathieson Chemical Corporation | Bossier City | S | Contact |
| Stauffer Chemical Company | Baton Rouge | RS | Contact |
| *MAINE* | | | |
| Northern Chemical Industries | Searsport | S | Contact |

| Company | Location | Raw materials | Process |
|---|---|---|---|
| *MARYLAND* | | | |
| The American Agricultural Chemical Co. | Baltimore | S | Chamber |
| Baugh Chemical Co. | Baltimore | S | Chamber |
| Bethlehem Steel Corporation | Sparrows Pt. | HP | Contact |
| W. R. Grace & Co.,<br>Davison Chemical Division | Baltimore | S | Contact |
| Olin Mathieson Chemical Corporation | Baltimore | S | Contact |
| F. S. Royster Guano Company | Baltimore | S | Chamber |
| U. S. Naval Powder Factory | Indian Head | S | Contact |
| *MASSACHUSETTS* | | | |
| The American Agricultural Chemical Co. | North Weymouth | S | Chamber |
| Monsanto Company | Everett | S | Contact |
| *MICHIGAN* | | | |
| Allied Chemical Corporation,<br>General Chemical Division | River Rouge | RS | Contact |
| The American Agricultural Chemical Co. | Detroit | S | Chamber |
| The American Agricultural Chemical Co. | Bay City | S | Contact |
| American Cyanamid Company | Kalamazoo | S | Contact |
| W. R. Grace & Co. | Detroit | S | Contact |
| E. I. du Pont de Nemours & Co. | Ecorse | RS | Contact |
| *MINNESOTA* | | | |
| North Star Chemical Company | Pine Bend | S | Contact |
| *MISSISSIPPI* | | | |
| Coastal Chemical Co., Inc. | Pascagoula | S | Contact |
| International Minerals & Chemical Corp. | Tupelo | S | Chamber |
| *MISSOURI* | | | |
| W. R. Grace & Co.,<br>Davison Chemical Division | Joplin | S | Contact |
| National Lead Company | St. Louis (Carondelet) | S | Contact |
| *MONTANA* | | | |
| The Anaconda Company | Anaconda | B | Contact |
| *NEVADA* | | | |
| The Anaconda Company | Yerington | Sc | Contact |
| *NEW JERSEY* | | | |
| Allied Chemical Corporation,<br>General Chemical Division | Elizabeth | RS | Contact |
| The American Agricultural Chemical Co. | Carteret | S | Chamber |
| American Cyanamid Company | Bound Brook | S | Contact |
| American Cyanamid Company | Warners | S | Contact |
| Armour and Company | Carteret | S | Chamber |
| Essex Chemical Corporation | Newark | S | Contact |
| Essex Chemical Corporation | Paulsboro | RS | Contact |
| E. I. du Pont de Nemours & Co. | Deepwater | S | Contact |
| E. I. du Pont de Nemours & Co. | Grasselli | S | Contact |
| E. I. du Pont de Nemours & Co. | Gibbstown | S | Contact |
| Koppers Company, Inc. | Kearney | HS | Contact |
| National Lead Company | Sayreville | S | Contact |

| Company | Location | Raw materials | Process |
|---|---|---|---|
| *NEW MEXICO* | | | |
| The Anaconda Company | Grants | S | Contact |
| Climax Chemical Company | Hobbs (Monument) | HS | Contact |
| Kermac Nuclear Fuels Corporation | Grants | S | Contact |
| *NEW YORK* | | | |
| Allied Chemical Corporation, General Chemical Division | Buffalo | HRS | Contact |
| The American Agricultural Chemical Co. | Buffalo | S | Chamber |
| Eastman Kodak Company | Rochester | S | Contact |
| *NORTH CAROLINA* | | | |
| Acme Chemical Industries | Acme | S | Contact |
| Acme Fertilizer Company | Acme | S | Chamber |
| The American Agricultural Chemical Co. | Greensboro | S | Chamber |
| Armour and Company | Greensboro | S | Chamber |
| Armour and Company | Navassa | S | Chamber |
| Swift & Company | Wilmington | S | Contact |
| V-C Chemical Co. — Division of Socony Mobil Oil Company | Navassa | S | Contact |
| V-C Chemical Co. — Division of Socony Mobil Oil Company | Selma | S | Chamber |
| *OHIO* | | | |
| Allied Chemical Corporation, General Chemical Division | Painesville | S | Contact |
| Allied Chemical Corporation, General Chemical Division | Cleveland | S | Contact |
| American Cyanamid Company | Hamilton | S | Contact |
| The American Agricultural Chemical Co. | Cleveland | S | Chamber |
| The American Agricultural Chemical Co. | Cincinnati (St.Bern'd) | S | Chamber |
| The American Agricultural Chemical Co. | Cairo | S | Contact |
| American Zinc Oxide Company (Farmer's Fertilizer Company) | Columbus | S | Chamber |
| Armour and Company | Sandusky | S | Chamber |
| E. I. du Pont de Nemours & Co. | Cleveland | S | Contact |
| E. I. du Pont de Nemours & Co. | Fort Hill | S | Contact |
| International Minerals & Chemical Corp. | Lockland | S | Contact |
| Marion Plant Life Fertilizer Co. | Sandusky | S | Contact |
| Minnesota Mining and Manufacturing Co. | Copley | BS | Contact |
| F. S. Royster Guano Company | Toledo | S | Contact |
| Smith Douglass Co., Inc. | Columbus | S | Chamber |
| V-C Chemical Co. — Division of Socony Mobil Oil Company | Cincinnati (St.Bern'd) | S | Contact |
| *OKLAHOMA* | | | |
| National Zinc Co. | Bartlesville | Z | Contact |
| Ozark Mahoning Co. | Tulsa | S | Contact |
| *PENNSYLVANIA* | | | |
| Allied Chemical Corporation, General Chemical Division | Newell | PRS | Contact |
| The Atlantic Refining Company | Philadelphia | HRS | Contact |

| Company | Location | Raw materials | Process |
|---|---|---|---|
| E. I. du Pont de Nemours & Co. | Cornwell Hts. | S | Contact |
| The New Jersey Zinc Company | Palmerton | Z | Contact |
| Chas. Pfizer & Co., C. K. Williams & Co. Division | Easton | B | Contact |
| Pittsburgh Coke & Chemical Company | Neville Island | HS | Contact |
| Rohm & Haas Company | Bridesburgh (Philadelphia) | S | Contact |
| St. Joseph Lead Company | Josephtown | Z | Contact |
| United States Steel Corporation, American Steel and Wire Division | Donora | S | Chamber |
| Witco Chemical Company, Inc. (Conneborn Chem. & Refining Corp.) | Petrolia | RS | Contact |
| *RHODE ISLAND* | | | |
| Heyden Newport Chemical Corporation (Rumford Chemical Works) | Rumford | S | Contact |
| *SOUTH CAROLINA* | | | |
| The American Agricultural Chemical Co. | Charleston | S | Chamber |
| Anderson Fertilizer Co., Inc. | Anderson | S | Chamber |
| W. R. Grace & Co., Davison Chemical Division | Charleston | S | Contact |
| International Minerals and Chemical Corporation | Spartanburg | S | Chamber |
| Planters Fertilizer & Phosphate Co. | Charleston | PS | Chamber |
| F. S. Royster Guano Company | Charleston | S | Chamber |
| V-C Chemical Co. — Division of Socony Mobil Oil Company | Charleston | S | Chamber |
| V-C Chemical Co. — Division of Socony Mobil Oil Company | Greenville | S | Chamber |
| *TENNESSEE* | | | |
| Armour and Company | Nashville | S | Chamber |
| Tennessee Corporation | Copperhill | P | Contact |
| Tennessee Corporation | Copperhill | P | Chamber |
| V-C Chemical Co. — Division of Socony Mobil Oil Company | Memphis | S | Chamber |
| Volunteer Ordnance Works | Tyner | S | Contact |
| *TEXAS* | | | |
| American Smelting & Refining Company | Corpus Christi | Z | Contact |
| Armour and Company | Houston | S | Chamber |
| E. I. du Pont de Nemours & Co. | La Porte | RS | Contact |
| Gulf Oil Corporation | Port Arthur | HRS | Contact |
| Olin Mathieson Chemical Corporation | Beaumont | HRS | Contact |
| Olin Mathieson Chemical Corporation | Port Arthur | S | Contact |
| Olin Mathieson Chemical Corporation | Pasadena | S | Contact |
| Shamrock Oil & Gas Corporation | Sunray | RS | Contact |
| Smith Douglass Co., Inc. | Texas City | RS | Contact |
| Stauffer Chemical Company | Fort Worth | S | Contact |
| Stauffer Chemical Company | Houston | RS | Contact |
| Stauffer Chemical Company | Baytown | HRS | Contact |

| Company | Location | Raw materials | Process |
|---|---|---|---|
| *UTAH* | | | |
| Garfield Chemical & Mfg. Corp. (Kennecott Copper Corp.) | Garfield | C | Contact |
| Texas Zinc Minerals Corporation | Mexican Hat | S | Contact |
| United States Steel Corporation | Provo (Geneva) | H | Contact |
| *VIRGINIA* | | | |
| Allied Chemical Corporation, General Chemical Division | Pulaski | S | Contact |
| Allied Chemical Corporation, General Chemical Division | Front Royal | S | Contact |
| American Cyanamid Company | Piney River | S | Contact |
| E. I. du Pont de Nemours & Co. | James River | S | Contact |
| Hercules Powder Company, Inc. (Radford Ordnance Works) | Radford | S | Contact |
| W. R. Grace & Co., Davison Chemical Division | Norfolk (Money Pt.) | S | Chamber |
| F. S. Royster Guano Company | Norfolk | S | Chamber |
| Smith Douglass Co., Inc. | Norfolk | S | Contact |
| Swift & Company | Norfolk | S | Contact |
| V-C Chemical Co. — Division of Socony Mobil Oil Company | Lynchburg | S | Chamber |
| V-C Chemical Co. — Division of Socony Mobil Oil Co. | Richmond | S | Chamber |
| Weaver Fertilizer Company | Norfolk | S | Contact |
| *WASHINGTON* | | | |
| Allied Chemical Corporation, General Chemical Division | Anacortes | HRS | Contact |
| American Smelting & Refining Company | Tacoma | C | Contact |
| *WEST VIRGINIA* | | | |
| Allied Chemical Corporation, General Chemical Division | Nitro | S | Contact |
| Union Carbide Corporation | S. Charleston | S | Contact |
| *WISCONSIN* | | | |
| Badger Ordnance Works | Baraboo | S | Contact |
| E. I. du Pont de Nemours & Co. | Barksdale | S | Contact |
| F. S. Royster Guano Company | Madison | S | Contact |
| *WYOMING* | | | |
| Susquehanna-Western, Inc. | Riverton | S | Contact |
| Western Nuclear Co., Inc. | Jeffrey City | S | Contact |

# APPENDIX E: PHYSICAL DATA

TABLE E1. PHYSICAL DATA FOR SULFURIC ACID, 0-93% *(23)*

| Bé° | Sp. gr. | Tw.° | Percent $H_2SO_4$ | Weight of 1 cu ft, lb avdp | Percent O. V. | Pounds O.V. in 1 cu ft | Freezing (Melting) Point, °F |
|---|---|---|---|---|---|---|---|
| 0 | 1.0000 | 0.0 | 0.00 | 62.37 | 0.00 | 0.00 | 32.0 |
| 1 | 1.0069 | 1.4 | 1.02 | 62.80 | 1.09 | .68 | 31.2 |
| 2 | 1.0140 | 2.8 | 2.08 | 63.24 | 2.23 | 1.41 | 30.5 |
| 3 | 1.0211 | 4.2 | 3.13 | 63.69 | 3.36 | 2.14 | 29.8 |
| 4 | 1.0284 | 5.7 | 4.21 | 64.14 | 4.52 | 2.90 | 28.9 |
| 5 | 1.0357 | 7.1 | 5.28 | 64.60 | 5.67 | 3.66 | 28.1 |
| 6 | 1.0432 | 8.6 | 6.37 | 65.06 | 6.84 | 4.45 | 27.2 |
| 7 | 1.0507 | 10.1 | 7.45 | 65.53 | 7.99 | 5.24 | 26.3 |
| 8 | 1.0584 | 11.7 | 8.55 | 66.01 | 9.17 | 6.06 | 25.1 |
| 9 | 1.0662 | 13.2 | 9.66 | 66.50 | 10.37 | 6.89 | 24.0 |
| 10 | 1.0741 | 14.8 | 10.77 | 66.99 | 11.56 | 7.74 | 22.8 |
| 11 | 1.0821 | 16.4 | 11.89 | 67.49 | 12.76 | 8.61 | 21.5 |
| 12 | 1.0902 | 18.0 | 13.01 | 68.00 | 13.96 | 9.49 | 20.0 |
| 13 | 1.0985 | 19.7 | 14.13 | 68.51 | 15.16 | 10.39 | 18.3 |
| 14 | 1.1069 | 21.4 | 15.25 | 69.04 | 16.36 | 11.30 | 16.6 |
| 15 | 1.1154 | 23.1 | 16.38 | 69.57 | 17.58 | 12.23 | 14.7 |
| 16 | 1.1240 | 24.8 | 17.53 | 70.10 | 18.81 | 13.19 | 12.6 |
| 17 | 1.1328 | 26.6 | 18.71 | 70.65 | 20.08 | 14.18 | 10.2 |
| 18 | 1.1417 | 28.3 | 19.89 | 71.21 | 21.34 | 15.20 | 7.7 |
| 19 | 1.1508 | 30.2 | 21.07 | 71.78 | 22.61 | 16.23 | 4.8 |
| 20 | 1.1600 | 32.0 | 22.25 | 72.35 | 23.87 | 17.27 | + 1.6 |
| 21 | 1.1694 | 33.9 | 23.43 | 72.94 | 25.14 | 18.34 | — 1.8 |
| 22 | 1.1789 | 35.8 | 24.61 | 73.53 | 26.41 | 19.42 | — 6.0 |
| 23 | 1.1885 | 37.7 | 25.81 | 74.13 | 27.69 | 20.53 | —11 |
| 24 | 1.1983 | 39.7 | 27.03 | 74.74 | 29.00 | 21.68 | —16 |
| 25 | 1.2083 | 41.7 | 28.28 | 75.36 | 30.34 | 22.87 | —23 |
| 26 | 1.2185 | 43.7 | 29.53 | 76.00 | 31.69 | 24.08 | —30 |
| 27 | 1.2288 | 45.8 | 30.79 | 76.64 | 33.04 | 25.32 | —39 |
| 28 | 1.2393 | 47.9 | 32.05 | 77.30 | 34.39 | 26.58 | —49 |
| 29 | 1.2500 | 50.0 | 33.33 | 77.96 | 35.76 | 27.88 | —61 |
| 30 | 1.2609 | 52.2 | 34.63 | 78.64 | 37.16 | 29.22 | —74 |
| 31 | 1.2719 | 54.4 | 35.93 | 79.33 | 38.55 | 30.58 | —82 |
| 32 | 1.2832 | 56.6 | 37.26 | 80.03 | 39.98 | 32.00 | —96 |
| 33 | 1.2946 | 58.9 | 38.58 | 80.74 | 41.40 | 33.42 | —97 |
| 34 | 1.3063 | 61.3 | 39.92 | 81.47 | 42.83 | 34.90 | —91 |
| 35 | 1.3182 | 63.6 | 41.27 | 82.22 | 44.28 | 36.41 | —81 |
| 36 | 1.3303 | 66.1 | 42.63 | 82.97 | 45.74 | 37.95 | —70 |
| 37 | 1.3426 | 68.5 | 43.99 | 83.74 | 47.20 | 39.53 | —60 |
| 38 | 1.3551 | 71.0 | 45.35 | 84.52 | 48.66 | 41.13 | —53 |
| 39 | 1.3679 | 73.6 | 46.72 | 85.32 | 50.13 | 42.77 | —47 |
| 40 | 1.3810 | 76.2 | 48.10 | 86.13 | 51.61 | 44.45 | —41 |
| 41 | 1.3942 | 78.8 | 49.47 | 86.96 | 53.08 | 46.16 | —35 |
| 42 | 1.4078 | 81.6 | 50.87 | 87.80 | 54.58 | 47.92 | —31 |
| 43 | 1.4216 | 84.3 | 52.26 | 88.67 | 56.07 | 49.72 | —27 |
| 44 | 1.4356 | 87.1 | 53.66 | 89.54 | 57.58 | 51.56 | —23 |
| 45 | 1.4500 | 90.0 | 55.07 | 90.44 | 59.09 | 53.44 | —20 |
| 46 | 1.4646 | 92.9 | 56.48 | 91.35 | 60.60 | 55.36 | —14 |
| 47 | 1.4796 | 95.9 | 57.90 | 92.28 | 62.13 | 57.33 | —15 |
| 48 | 1.4948 | 99.0 | 59.32 | 93.23 | 63.65 | 59.34 | —18 |
| 49 | 1.5104 | 102.1 | 60.75 | 94.20 | 65.18 | 61.40 | —22 |
| 50 | 1.5263 | 105.3 | 62.18 | 95.20 | 66.72 | 63.52 | —27 |

TABLE E1 (Continued)

| Bé° | Sp. gr. | Tw.° | Percent $H_2SO_4$ | Weight of 1 cu ft, lb avdp | Percent O. V. | Pounds O. V. in 1 cu ft | Freezing (Melting) Point, °F |
|---|---|---|---|---|---|---|---|
| 51 | 1.5426 | 108.5 | 63.66 | 96.21 | 68.31 | 65.72 | —33 |
| 52 | 1.5591 | 111.8 | 65.13 | 97.24 | 69.89 | 67.96 | —39 |
| 53 | 1.5761 | 115.2 | 66.63 | 98.30 | 71.50 | 70.28 | —49 |
| 54 | 1.5934 | 118.7 | 68.13 | 99.38 | 73.11 | 72.66 | —59 |
| 55 | 1.6111 | 122.2 | 69.65 | 100.48 | 74.74 | 75.10 | .... Below —40 |
| 56 | 1.6292 | 125.8 | 71.17 | 101.61 | 76.37 | 77.60 | .... |
| 57 | 1.6477 | 129.5 | 72.75 | 102.77 | 78.07 | 80.23 | .... |
| 58 | 1.6667 | 133.3 | 74.36 | 103.95 | 79.79 | 82.95 | .... |
| 59 | 1.6860 | 137.2 | 75.99 | 105.16 | 81.54 | 85.75 | — 7 |
| 60 | 1.7059 | 141.2 | 77.67 | 106.40 | 83.35 | 88.68 | +12.6 |
| 61 | 1.7262 | 145.2 | 79.43 | 107.66 | 85.23 | 91.76 | 27.3 |
| 62 | 1.7470 | 149.4 | 81.30 | 108.96 | 87.24 | 95.06 | 39.1 |
| 63 | 1.7683 | 153.7 | 83.34 | 110.29 | 89.43 | 98.63 | 46.1 |
| 64 | 1.7901 | 158.0 | 85.66 | 111.65 | 91.92 | 102.63 | 46.4 |
| 64¼ | 1.7957 | 159.1 | 86.33 | 112.00 | 92.64 | 103.75 | 43.6 |
| 64½ | 1.8012 | 160.2 | 87.04 | 112.34 | 93.40 | 104.93 | 41.1 |
| 64¾ | 1.8068 | 161.4 | 87.81 | 112.69 | 94.23 | 106.19 | 37.9 |
| 65 | 1.8125 | 162.5 | 88.65 | 113.05 | 95.13 | 107.54 | 33.1 |
| 65¼ | 1.8182 | 163.6 | 89.55 | 113.40 | 96.10 | 108.97 | 24.6 |
| 65½ | 1.8239 | 164.8 | 90.60 | 113.76 | 97.22 | 110.60 | 13.4 |
| 65¾ | 1.8297 | 165.9 | 91.80 | 114.12 | 98.51 | 112.42 | — 1 |
| 66 | 1.8354 | 167.1 | 93.19 | 114.47 | 100.00 | 114.47 | —29 |

Specific gravity determinations were made at 60° F, compared with water at 60° F.

From the specific gravities, the corresponding degrees Baumé were calculated by the following formula:

$$\text{Baumé} = 145 - \frac{145}{\text{sp. gr.}}$$

Baumé hydrometers for use with this table must be graduated by the above formula, which should always be printed on the scale.

66° Baumé = sp. gr. 1.8354
1 cu ft water at 60° F weighs 62.37 lb avoirdupois

$H_2SO_4$ = 100 percent

|  | $H_2SO_4$ | O. V. | 60° |
|---|---|---|---|
| O. V. | 93.19 | 100.00 | 119.98 |
| 60° | 77.67 | 83.35 | 100.00 |
| 50° | 62.18 | 66.72 | 80.06 |

Percentage compositions of acids stronger than 66° Bé should be determined by chemical analysis.

## TABLE E1 (Continued)

### APPROXIMATE BOILING POINTS

| | |
|---|---|
| 50° Bé, | 295°F |
| 60° | 336 |
| 61° | 400 |
| 62° | 415 |
| 63° | 432 |
| 64° | 451 |
| 65° | 485 |
| 66° | 538 |

### FIXED POINTS

| Sp. gr. | Percent $H_2SO_4$ | Sp. gr. | Percent $H_2SO_4$ |
|---|---|---|---|
| 1.0000 | .00 | 1.5281 | 62.34 |
| 1.0048 | .71 | 1.5440 | 63.79 |
| 1.0347 | 5.14 | 1.5748 | 66.51 |
| 1.0649 | 9.48 | 1.6272 | 71.00 |
| 1.0992 | 14.22 | 1.6679 | 74.46 |
| 1.1353 | 19.04 | 1.7044 | 77.54 |
| 1.1736 | 23.94 | 1.7258 | 79.40 |
| 1.2105 | 28.55 | 1.7472 | 81.32 |
| 1.2513 | 33.49 | 1.7700 | 83.47 |
| 1.2951 | 38.64 | 1.7959 | 86.36 |
| 1.3441 | 44.15 | 1.8117 | 88.53 |
| 1.3947 | 49.52 | 1.8194 | 89.75 |
| 1.4307 | 53.17 | 1.8275 | 91.32 |
| 1.4667 | 56.68 | 1.8354 | 93.19 |
| 1.4822 | 58.14 | | |

### ALLOWANCE FOR TEMPERATURE

| At Bé | Bé, or | sp. gr. |
|---|---|---|
| 10° | 0.029° | 0.00023 = 1°F. |
| 20° | 0.036° | 0.00034 = 1° |
| 30° | 0.035° | 0.00039 = 1° |
| 40° | 0.031° | 0.00041 = 1° |
| 50° | 0.028° | 0.00045 = 1° |
| 60° | 0.026° | 0.00053 = 1° |
| 63° | 0.026° | 0.00057 = 1° |
| 66° | 0.0235° | 0.00054 = 1° |

| Percent 60° | Pounds 60° in 1 cu ft | Percent 50° | Pounds 50° in 1 cu ft |
|---|---|---|---|
| 61.93 | 53.34 | 77.36 | 66.63 |
| 63.69 | 55.39 | 79.56 | 69.19 |
| 65.50 | 57.50 | 81.81 | 71.83 |
| 67.28 | 59.66 | 84.05 | 74.53 |
| 69.09 | 61.86 | 86.30 | 77.27 |
| 70.90 | 64.12 | 88.56 | 80.10 |
| 72.72 | 66.43 | 90.83 | 82.98 |
| 74.55 | 68.79 | 93.12 | 85.93 |
| 76.37 | 71.20 | 95.40 | 88.94 |
| 78.22 | 73.68 | 97.70 | 92.03 |
| 80.06 | 76.21 | 100.00 | 95.20 |
| 81.96 | 78.85 | 102.38 | 98.50 |
| 83.86 | 81.54 | 104.74 | 101.85 |
| 85.79 | 84.33 | 107.15 | 105.33 |
| 87.72 | 87.17 | 109.57 | 108.89 |
| 89.67 | 90.10 | 112.01 | 112.55 |
| 91.63 | 93.11 | 114.46 | 116.30 |
| 93.67 | 96.26 | 117.00 | 120.24 |
| 95.74 | 99.52 | 119.59 | 124.31 |
| 97.84 | 102.89 | 122.21 | 128.52 |
| 100.00 | 106.40 | 124.91 | 132.91 |
| 102.27 | 110.10 | 127.74 | 137.52 |
| 104.67 | 114.05 | 130.75 | 142.47 |
| 107.30 | 118.34 | 134.03 | 147.82 |
| 110.29 | 123.14 | 137.76 | 153.81 |
| 111.15 | 124.49 | 138.84 | 155.50 |
| 112.06 | 125.89 | 139.98 | 157.25 |
| 113.05 | 127.40 | 141.22 | 159.14 |
| 114.14 | 129.03 | 142.57 | 161.17 |
| 115.30 | 130.75 | 144.02 | 163.32 |
| 116.65 | 132.70 | 145.71 | 165.76 |
| 118.19 | 134.88 | 147.63 | 168.48 |
| 119.98 | 137.34 | 149.87 | 171.56 |

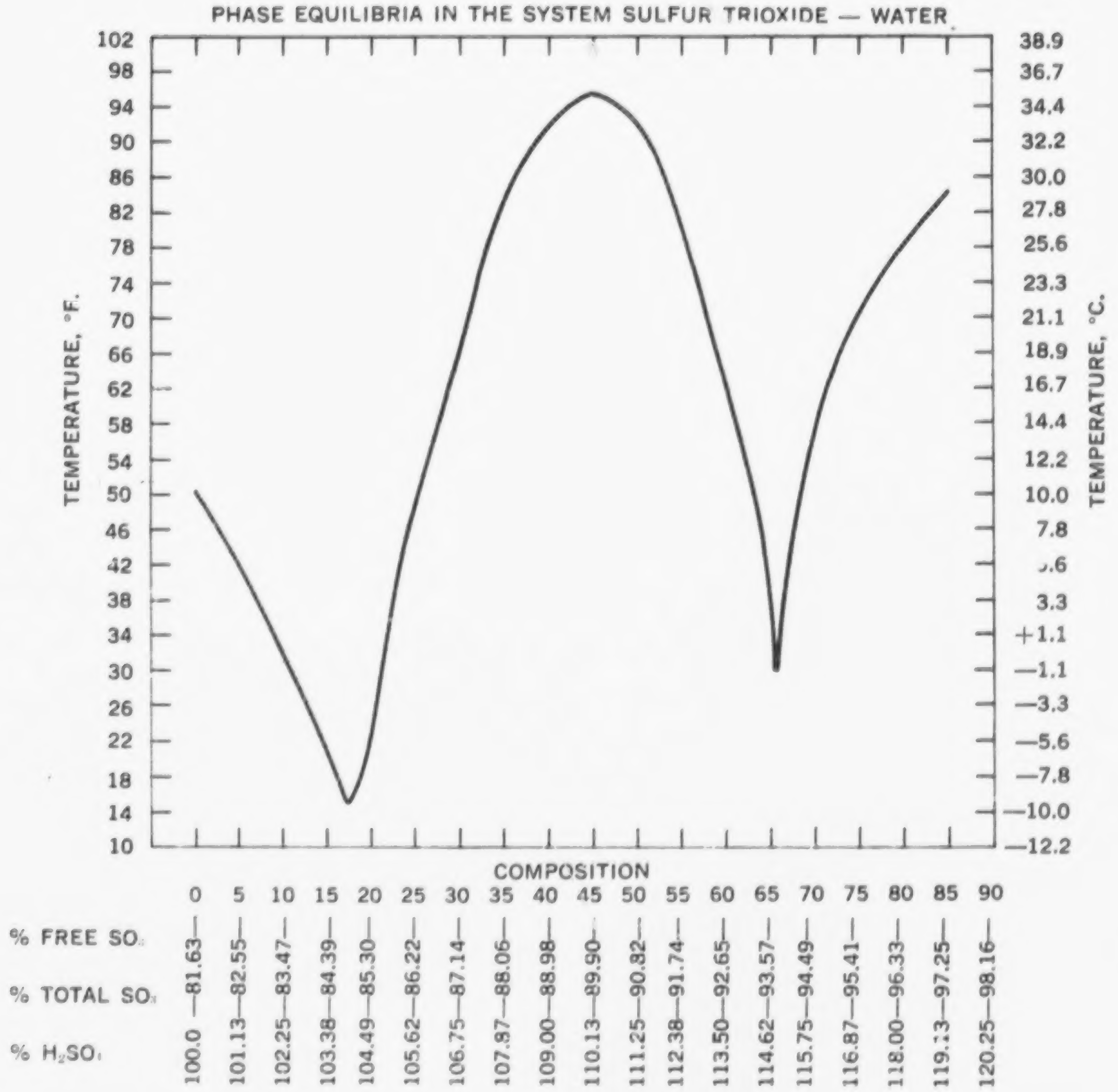
## TABLE E2. PHYSICAL DATA FOR SULFURIC ACID, 94-100% (*24*)

| Percent $H_2SO_4$ | Sp. gr. | Wt. of 1 cu ft, lb avdp | Percent O. V. | Pounds O. V. in 1 cu ft | Freezing Point | |
|---|---|---|---|---|---|---|
| | | | | | °F | °C |
| 94.0 | 1.8381 | 114.64 | 100.87 | 115.64 | —28.1 | —33.4 |
| 95.0 | 1.8407 | 114.80 | 101.94 | 117.03 | —11.7 | —24.3 |
| 96.0 | 1.8427 | 114.93 | 103.01 | 118.39 | + 5.7 | —14.6 |
| 97.0 | 1.8437 | 114.99 | 104.09 | 119.69 | 17.1 | — 8.3 |
| 97.5 | 1.8439 | 115.00 | 104.63 | 120.32 | 23.2 | — 4.9 |
| 98.0 | 1.8437 | 114.99 | 105.16 | 120.92 | 28.6 | — 1.9 |
| 99.0 | 1.8424 | 114.91 | 106.23 | 122.07 | 39.9 | + 4.4 |
| 100.0 | 1.8391 | 114.70 | 107.31 | 123.08 | 50.6 | 10.35 |

| Percent 60° | Pounds 60° in 1 cu ft | Percent 50° | Pounds 50° in 1 cu ft | Percent $SO_3$ | Pounds $SO_3$ in 1 cu ft |
|---|---|---|---|---|---|
| 121.02 | 138.74 | 151.17 | 173.30 | 76.73 | 87.97 |
| 122.31 | 140.41 | 152.78 | 175.39 | 77.55 | 89.03 |
| 123.60 | 142.05 | 154.39 | 177.44 | 78.37 | 90.07 |
| 124.89 | 143.61 | 156.00 | 179.38 | 79.18 | 91.05 |
| 125.53 | 144.34 | 156.81 | 180.31 | 79.59 | 91.53 |
| 126.17 | 145.08 | 157.61 | 181.24 | 80.00 | 91.99 |
| 126.46 | 145.32 | 159.22 | 182.96 | 80.82 | 92.87 |
| 128.75 | 147.68 | 160.82 | 184.46 | 81.63 | 93.63 |

### ALLOWANCE FOR TEMPERATURE

| | | | |
|---|---|---|---|
| At | 94% | 0.00054 sp. gr. = 1°F | 0.00097 sp. gr. = 1°C |
| | 96% | 0.00053 sp. gr. = 1° | 0.00095 sp. gr. = 1° |
| | 97.5% | 0.00052 sp. gr. = 1° | 0.00094 sp. gr. = 1° |
| | 100% | 0.00052 sp. gr. = 1° | 0.00094 sp. gr. = 1° |



| % FREE $SO_3$ | % TOTAL $SO_3$ | % $H_2SO_4$ |
|---|---|---|
| 0 | 81.63 | 100.0 |
| 5 | 82.55 | 101.13 |
| 10 | 83.47 | 102.25 |
| 15 | 84.39 | 103.38 |
| 20 | 85.30 | 104.49 |
| 25 | 86.22 | 105.62 |
| 30 | 87.14 | 106.75 |
| 35 | 88.06 | 107.87 |
| 40 | 88.98 | 109.00 |
| 45 | 89.90 | 110.13 |
| 50 | 90.82 | 111.25 |
| 55 | 91.74 | 112.38 |
| 60 | 92.65 | 113.50 |
| 65 | 93.57 | 114.62 |
| 70 | 94.49 | 115.75 |
| 75 | 95.41 | 116.87 |
| 80 | 96.33 | 118.00 |
| 85 | 97.25 | 119.13 |
| 90 | 98.16 | 120.25 |

Freezing points over the entire system were determined by the equilibrium method with purified oleum.

Determinations made at the Case School of Applied Science, Cleveland, Ohio, by S. H. Maron and H. F. Betz.

Figure E1 — Oleum freezing point diagram(*22*).

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